Primary Production in the Murderkill River

A Report to Kent County and Delaware DNREC on a project by

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1. Introduction

To assist in assessing the impact of the Kent County Sewage Treatment Plant on the ecology of the Murderkill River, a project was conducted measuring primary production. This project was one part of a cooperative effort between Kent County, Delaware and the Delaware Department of Natural Resources and Environmental Control (DNREC) that was carried out to develop TMDL levels for effluents from the sewage treatment plant that flow into the Murderkill River.

All sampling was conducted on the second monthly boat runs operated by DNREC. The boat runs were from the mouth of the Murderkill River on the Delaware Bay to the Route 12 bridge on Frederica Rd. Sampling was done by personnel from our laboratory (laboratory of Jonathan Sharp at the University of Delaware School of Marine Science and Policy in Lewes) and samples were collected at the same time as routine samples collected by DNREC. Sampling for this project was monthly from April 2007 through December 2008. Samples for this project were quickly returned to our laboratory in Lewes at the same time that the DNREC samples were returned to the DNREC laboratory in Dover. Efforts were made for the two sets of samples to be contemporaneous so that parameters measured by DNREC could be used in calculations for this project.

Over the past few centuries, coastal and estuarine waters of the world have experienced severe degradation from human pressure with some stabilization and recovery in recent years (e.g. review by Lotze et al. 2006). Often, the primary concern about the degradation is eutrophication from nutrient enrichment, especially by nitrogen (e.g. Nixon and Pilson 1983; Vitousek et al. 1996). The general characterization is of nutrients stimulating excess chlorophyll production that leads to hypoxia (e.g., Rabalais and Nixon 2002; Howarth and Marino 2006). This paradigm has been tempered with debate both for characterizing the problem and for assessing remedial action. The prominent view of nutrient eutrophication (e.g. Boesch et al. 2001; Pomeroy et al. 2007) has been challenged by the contention that the failure of consumption of primary production by higher trophic levels is the cause of degradation rather than excess production (e.g. Jackson et al. 2001; Newell et al. 2007). In addition to the influence of a single nutrient on primary producers, nutrient reactions with non-primary producers, multiple nutrient influences, and light influences are also important. The association of excess chlorophyll biomass leading to hypoxia is essentially a secondary biochemical oxygen demand (BOD), one caused by autochthonous sources. In addition, primary BOD, or oxygen depletion from allochthonous inputs, is important in estuaries and coastal waters (Mallin et al, 2006; Sharp, 2010).

The data from DNREC needed for interpretation include salinity, light penetration, total suspended sediments, dissolved oxygen, nutrients (nitrate plus nitrite, ammonium, phosphate, and silicate), and chlorophyll. The analyses performed by DNREC have been used routinely in Delaware Estuary research by our laboratory for the past 30 years (Sharp et al, 1982; Fogel et al, 1992; Sharp et al, 2009). Indirect and direct

methods comparisons have been made between our laboratory and DNREC. The indirect comparisons made for dissolved oxygen and nutrient measurements on the Delaware Estuary were included in a recent publication (Sharp, 2010). In addition, our laboratory protocols for analyses, and datasets have been accepted by US EPA through a QAPP submission in 2005.

Primary production was estimated with the "simulated *in-situ*" method established for open ocean research (Eppley and Sharp, 1975) and adapted for estuarine work (Pennock and Sharp, 1986; Yoshiyama and Sharp, 2006). This method, or a similar variant of it, has been adopted and used for routine primary production research internationally. It has been used consistently in the Delaware Estuary for over 25 years and DNREC has adopted the method for routine Boat Run monitoring in Delaware Estuary for DRBC. The method used previously required the radioactive isotope, ^{14}C, for tagging. Because of restrictions in use of radio-isotopes, the method has been limited in how incubations can be accomplished. For the past several years, we have experimented in our laboratory with use of the stable heavy isotope, ^{13}C, for primary production (Parker, 2004) and a paper in preparation (Parker et al, 2011), shows that the ^{14}C and ^{13}C tagging methods can give identical results.

2. Sampling and Parameters Measured In Our Laboratory and Those Used From DNREC Measurements

A small trailered outboard motor boat was put in the river at the wharf at Bowers Beach. This DNREC boat was used for a run up the Murderkill River with samples from the tidal length of the river to the intersection of the river with the Route 12 bridge (Frederica Road). A total of 7 stations were sampled on each run with a duplicate sample at the last for 8 sampling sites (Figure 2.1). The 8 samples are listed for each sampling date. They are numbered sequentially; the DNREC 6-digit station numbers and descriptive names of the sampling sites are also given below.

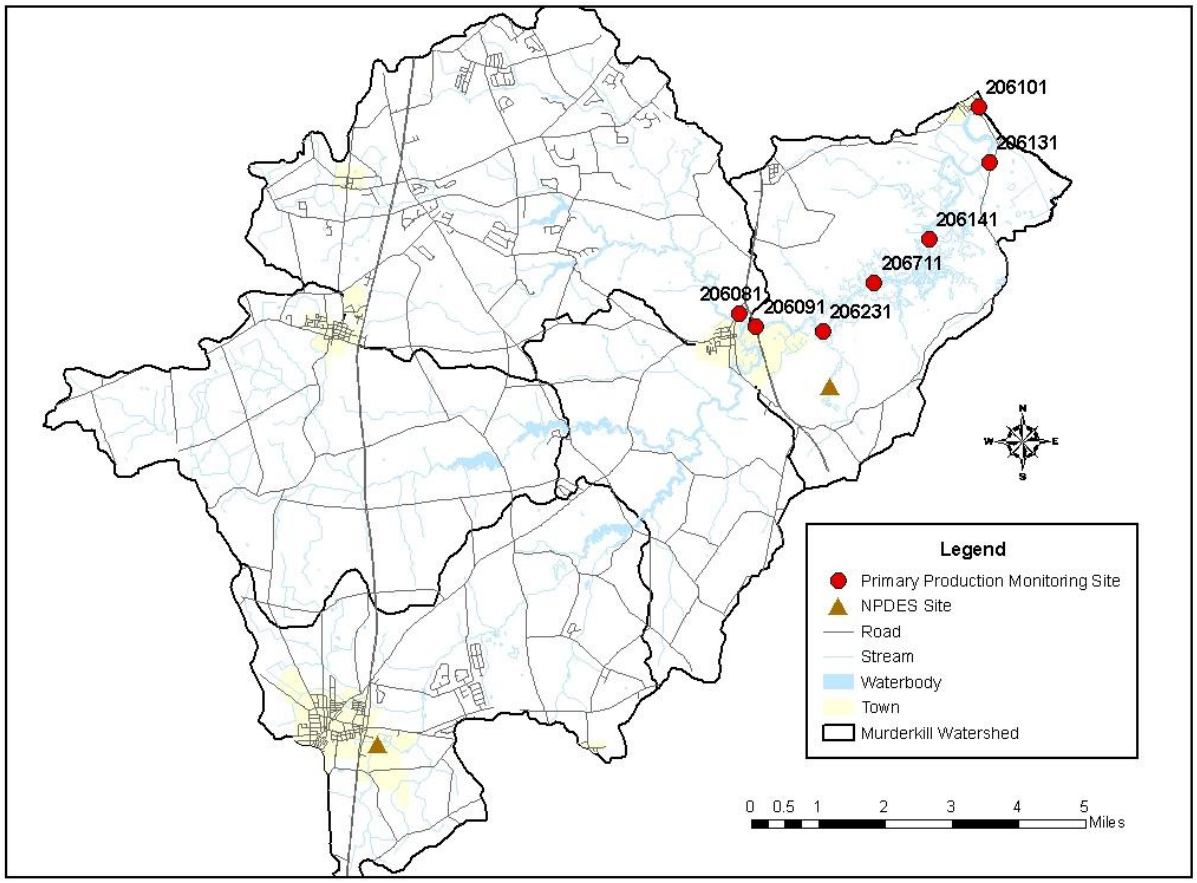

Figure 2.1. Sampling sites for primary production study. Sites are identified with the DNREC 5-digit sampling code. See listing below for our station numbers and description.

Station 10 = 206101 – Bowers Beach wharf
Station 11 = 206131 – Webb's Landing
Station 12 = 206141 – Milford Neck
Station 13 = 206711 – 4.45 river mile
Station 14 = 206231 – confluence of Kent County WWTP
Station 15 = 206091 – Bay Road (Rt 1/113)
Station 16 = 206081 – Frederica Rd (Rt 12)
Station 17 = replicate of 206081

DNREC personnel measured temperature and salinity with a hand-held CTD (conductivity, temperature, depth) system, measured light attenuation with a Secchi Disc, and collected several separate water samples to be returned to the laboratory for analyses. Personnel from our laboratory also collected water samples to return to the laboratory for analyses and for incubations to measure primary production.

Data from DNREC that were used in this report are listed in tables in section 5 below along with the reason that they are used in the report. In section 3 below, the routine analyses and incubation experiments performed in our laboratory are described and explained. Section 4 gives tables of primary production data with explanation of the individual parameters.

Light penetration can be measured using a quantum energy meter or a Secchi Disc; a detailed comparison of the two methods in the Delaware Estuary for determination of the photic zone depth shows them to be comparable (Sharp et al, 2009). The routine DNREC sampling included measurement of light penetration with the Secchi Disc. Unfortunately, this was not sufficiently sensitive in these very turbid waters, such that the difference between 0.2 and 0.3 meters for the disappearance depth was very difficult to determine. In the Delaware Estuary, a very tight relationship was found between the quantum meter estimates of light attenuation and the total suspended sediment concentration (TSS) in the water. The DNREC lab borrowed a quantum meter from USGS and made some light attenuation measurements. These were used to test the relationship with TSS. I received light profile data from DNREC sampling on 10 sampling dates in 2007 and 2008 and did analyses on these and Secchi depths.

The sampling dates were 04/24/2007, 05/14/2007, 05/30/2007, 06/26/2007, 07/10/2007, 09/05/2007, 10/22/2007, 06/09/2008, 11/12/2008, and 11/24/2008. On most of these sampling dates, light meter measurements were made at all seven of the stations, resulting in a total of 65 individual stations with measurements.

Individual light profiles were based on 4 to 9 depth readings with light measured within the visible spectrum as PAR (photosynthetic active region). The diffuse light attenuation coefficient (k) is calculated by plotting –ln PAR on the y-axis against the depth in meters. Independent of light intensity during the profile and independent of absolute light units, the plot should be linear. Most of the profiles had correlation coefficients (R^2) of 0.99. If the light intensity shifts during the profile from cloud or

shadow, outliers can occur; outliers are also often found at the surface due to slight error in depth (attempted reading at 1 inch below the surface) and at the bottom depth (from too little light). Thus, it is reasonable to empirically edit the plots to get the best linearity. Editing should be done cautiously and lightly; I found that I removed one depth on about half the plots (more rarely 2 or 3 removed in plots with 7-9 depths). With the editing, most of the plots had R^2 values of 0.99, while initial unedited plots were often in the 0.93 – 0.97 range. The Excel file "composite light calculations" includes all the data and all the plots (initial and edited). From the total of 65 light profiles, the k values ranged from a relatively clear water value of 1.53 m^{-1} to a very turbid value of 12.18 m^{-1}.

Examples of an unedited and edited plot are shown in Figure 2.2. It is interesting to note that on the 6/26/07 sampling, that no editing was needed – plots for each of the seven stations, based on 7-8 depths, gave initial R^2 values of at least 0.99. In contrast to that sampling, the 6/9/08 sampling, based on 6-9 depths, had 1-3 depths removed from each plot. Conditions at the time of the light measurements, plus attention paid to detail can make a large difference.

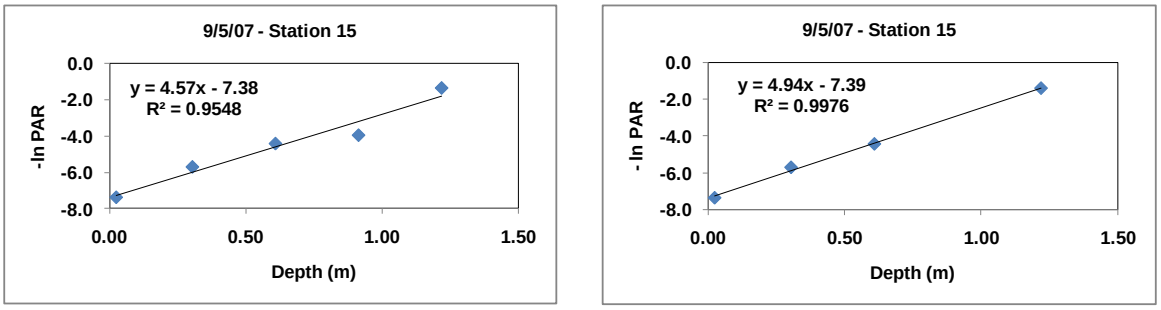

Figure 2.2. Unedited (left pane) and edited (right pane) light profiles for station 15 on 5 September 2007.

Individual depth profiles varied from relatively clear to very turbid (Figure 2.3) with attenuation coefficients as low as about 1 m^{-1} for clear to over 12 m^{-1} for turbid.

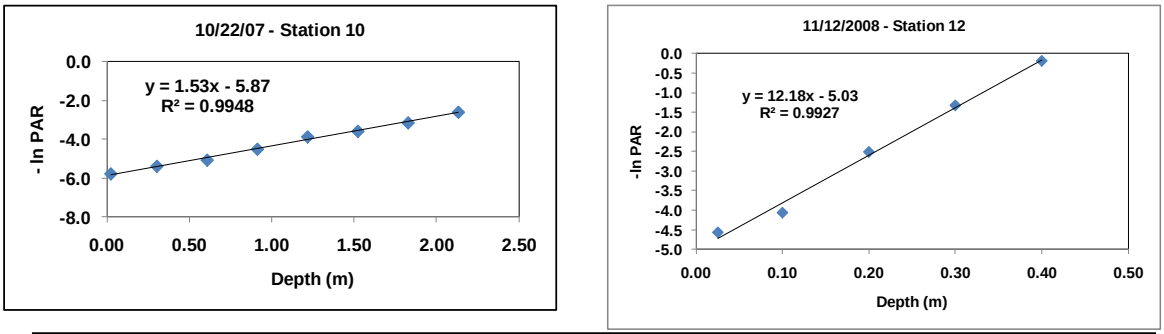

Figure 2.3. Examples of plots from relatively clear (left pane) and very turbid waters.

I also received TSS and Secchi depth data from these cruises, plus others in 2007 and 2008. I plotted the calculated k values against the TSS and the Secchi depths for regressions that might be used to estimate k values when the light meter was not used (Figure 2.4).

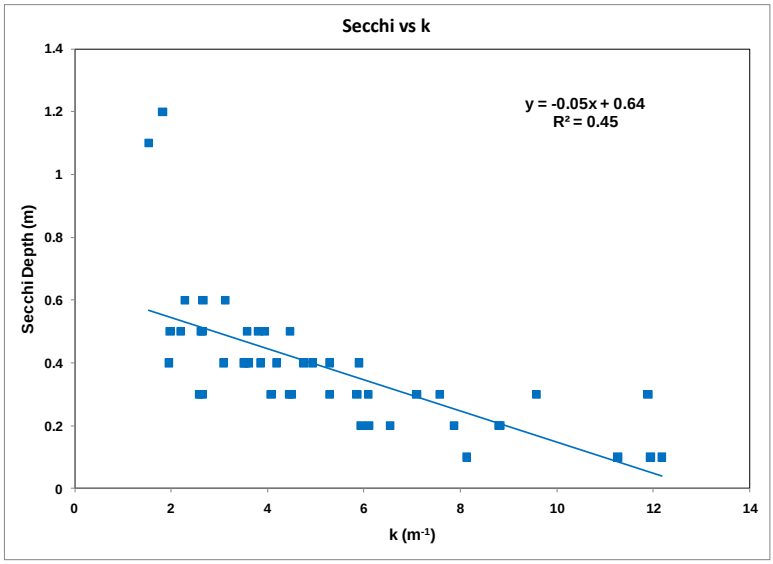

Figure 2.4. Plot of measured Secchi depth versus calculated k values.

The two Secchi depths greater than 1 m are outliers. They were removed from the plot; also, those depths most distant from the regression line were moved 0.05 m closer (higher or lower) with the idea that a reading of 0.3 m could be 0.25 or 0.35 m. These adjustments are arbitrary and are performed to show that measured disappearance depths in shallow turbid waters are not a fine enough metric for accurate light attenuation estimates. With these adjustments, the R^2 value is considerably improved in Figure 2.5.

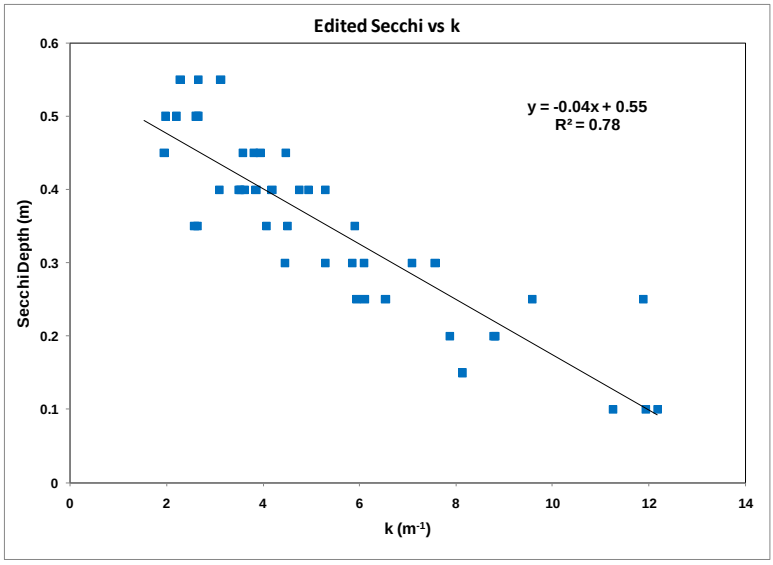

Figure 2.5. Plot of same data as shown in Figure 2.3 with two extreme values removed and adjustments of other readings by plus or minus 0.05 m to be closer to the regression line.

The plot of TSS vs k for all of the profiles is shown in Figure 2.6. The two data points highlighted as red circles are two samples for which the holding time had been exceeded prior to filtration for TSS (in these two cases, it would appear to not have caused bad data).

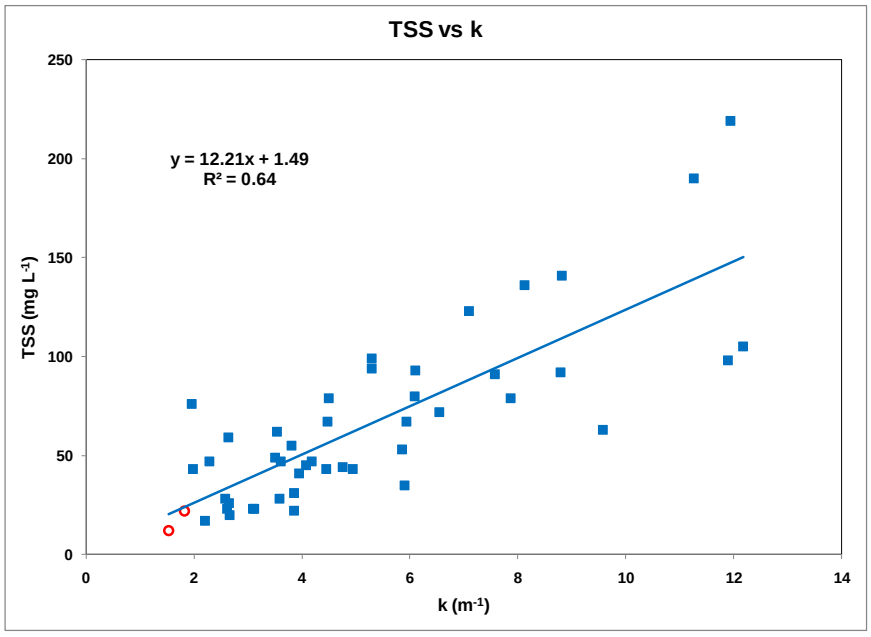

Figure 2.6. Plot of measured TSS concentrations versus calculated k values for all Murderkill River data that had paired measurements.

A similar plot from the Delaware Estuary (full length of the salinity gradient from DRBC station Marcus Hook to mouth of the bay) is shown Figure 2.7.; based on sampling from 1986 – 2003. The correlation coefficient is better than that for the Murderkill plot, partially due to a much larger sample n. However, the slope is remarkably similar and, in both cases, the intercept is close to zero. Therefore, it is possible to use the result from the regression to estimate an appropriate k value to use for stations where no light profiles were made. I recommend that we use the slope with an intercept of zero; thus the TSS value would be divided by 12 to estimate the k value.

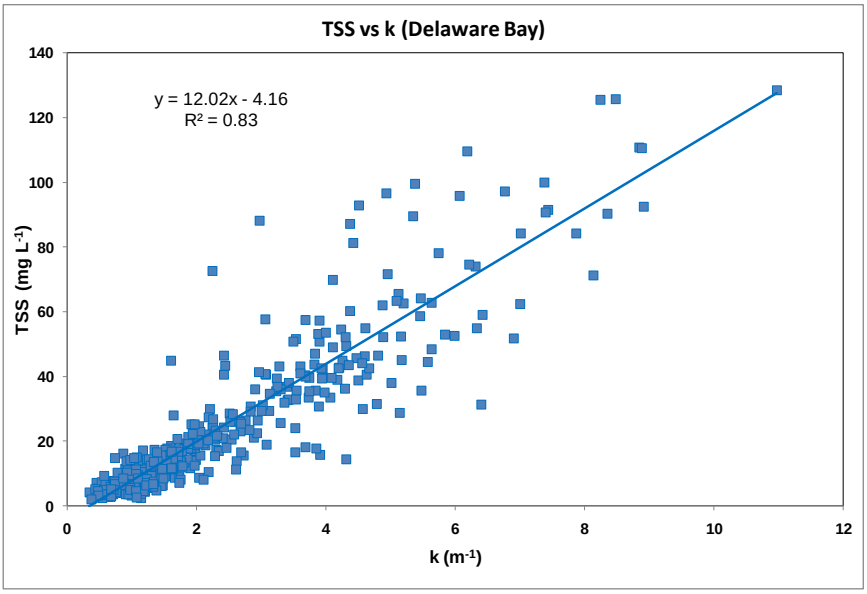

Figure 2.7. Plot of measured TSS concentrations versus calculated k values for samples from the full salinity gradient of the Delaware Estuary; collected in all seasons of the year from 1986 to 2003.

For the Delaware Estuary and probably many of the subtributary estuaries, at least for the Murderkill River, the TSS values do give a good approximation for light penetration. In the Delaware River urban region, we found that the relationship between TSS and k was not the same as within the salinity gradient of the estuary and attributed this difference to light attenuation from colored dissolved organic matter (CDOM). In a turbid estuarine region with a salinity gradient, the TSS values are so high and CDOM probably relatively low, that the TSS alone can give a good approximation for k. Therefore for all of the productivity measurements, we used a k derived by dividing the measured TSS concentration for that station by 12.

3. Incubation Experiments to Measure Primary Production

Primary production was estimated with the "simulated *in-situ*" method established for open ocean research (Eppley and Sharp, 1975) and adapted for estuarine work (Pennock and Sharp, 1986; Yoshiyama and Sharp, 2006). The modification in this project used the stable isotope ^{13}C instead of the radioactive isotope ^{14}C for the isotopic tag. The primary production method involved use of light penetration measurements, dissolved inorganic carbon (DIC) concentration of the water, and incubation of samples with isotopic carbon tracer. The DIC analysis is the high precision method of Freiderich et al (2002) that we have established in our laboratory (Sharp, et al, 2009).

A sample was taken of the same ambient water for the tracer incubation at the beginning of the experiment for determination of DIC. The DIC analysis was performed in our laboratory; the ambient DIC concentration was used along with amount of tracer added to quantify the isotopic composition of the ambient carbon pool. For the incubation, 7 aliquots of the water sample (in 60 ml bottles) were carefully poured out and the isotopic tracer was added. One bottle was immediately filtered as the time zero sample (T_0) and the other 6 were incubated in attenuation bags with decreasing light levels to simulate from 100% to 1.5% of the surface illumination. The samples were incubated for 24 hours and were then filtered as final samples ($T_{f\text{-}100}$ to $T_{f\text{-}1.5}$). The samples were analyzed in a gas chromatograph-mass spectrometer (GC-MS) system. The GC-MS gives the amount of carbon and nitrogen as well as isotopic composition of C and N; thus, a measure was also available of the ambient particulate carbon (PC) concentration; the T_0 PC. The ratio of ^{13}C over the more abundant ^{12}C isotope is the isotopic composition of the PC. The natural abundance of ^{13}C, confirmed with the T_0 measurement, is about 1.08 atom percent, but this varies slightly and the measured value was used. The T_f samples had enrichments in the range of 1.1 to 3.1 atom percent. The enrichment in the PC ($\Delta\ ^{13}C$) was the T_f atom percent minus the T_0 atom percent. This enrichment divided by the ambient pool DIC isotopic composition gives the uptake, v, in units of d^{-1}. The value of v times the measured PC ($T_f - T_0$) determines the C-uptake at each light level in the 24 hour day (µM C d^{-1}).

The C-uptake from the light series that was the highest was usually at 100% light, but occasionally, the 60% light level had higher uptake with the 100% light level being slightly less. This highest uptake is the P_{max}, the maximum volumetric uptake. The P_{max} divided by the ambient chlorophyll concentration (biomass, B) gives the ratio P/B. The P/B is often used as a physiological indicator to compare uptake, normalized to biomass of algae.

With the light attenuation, the carbon uptake was integrated over the photic zone (to 1% light penetration) so that the results are of "areal" primary production; that is total amount of carbon fixed under a square meter of water surface. The importance of areal production is that depending upon light absorption, photic zones in estuarine waters can range from less than 1 m to about 10 m (in the open ocean the photic zone can extend to 100m).

The simulated *in-situ* incubation method uses varying layers of screening to simulate light attenuation at depths in the water column with incubation being done on the deck of the ship. It is based on the concept that simple quantitative attenuation is a reasonable simulation of incubation at the depth in the water column represented by that percentage of attenuation. This concept has been verified with open ocean incubations (e.g., Eppley and Sharp, 1975). The attenuation bags that we use have values of 100, 60, 32, 15, 7.5, and 1.5% of surface illumination. Using the k value, calculated from TSS, for each station, the depths equivalent to the attenuation of each level is calculated from the k. For example, for the 60% light level, the depth = ln(0.6)/k. Using this approach, the depth of each of the 6 light levels (100% light depth is 0, ln(1) = 0), and for the 1% light level (= ln (0.01)/k) are calculated. The depth interval representing each of the light levels is calculated as the linear distance between the level above and that one below. The volumetric production for a light level (as mmoles m^{-3}, 1µmole L^{-1} = 1 mmole m^{-3}) is multiplied by the depth interval in m to get the areal production for that interval as mmol m^{-2} and the 6 intervals are added.

In using ^{13}C with the simulated *in-situ* method, an additional confirmation can be made of the accuracy of calculated carbon uptake when primary production is high. The mass spectrometer analysis of a sample gives the amount of carbon and nitrogen in the sample as well as the isotopic abundance of C and N in the sample. An example is shown in Figure 3.1for the change in particulate carbon (PC). The PC concentration in the samples increased significantly above the T_0 concentration. The final concentration at the 100% light level minus the T_0 concentration is the amount of carbon produced (PC growth) at full sunlight. In summer, with high primary production, the 100% light carbon uptake and PC growth was often in the 50 to 200 µM C range.

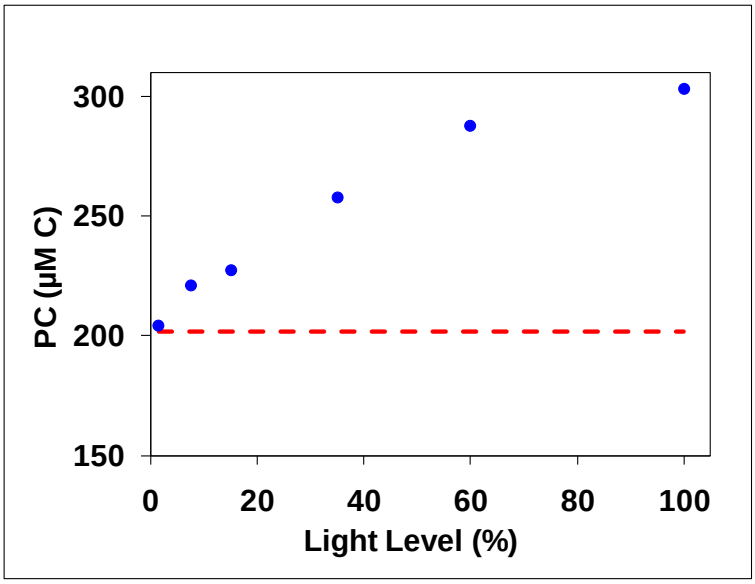

Figure 3.1. Particulate carbon concentrations at time zero (dashed red line) and after incubation at 6 light levels (blue dots). Data from station 10 in July 2007.

The summer production values were highest of the year. In Figure 3.2 below, the PC growth is compared to the carbon uptake calculated with ^{13}C for the 8 stations in four summer samplings. The precision of PC measurements is not much better than ± 10% and while the PC growth is treated as growth of phytoplankton by photosynthesis, potentially bacterial growth and increase of non-living particulate matter can also occur in the 24 hour incubation. Thus, the slope of 0.89 is close to ideal slope of 1, the intercept of -18 is not far from zero, and the regression coefficient of 0.75 is a relatively good fit.

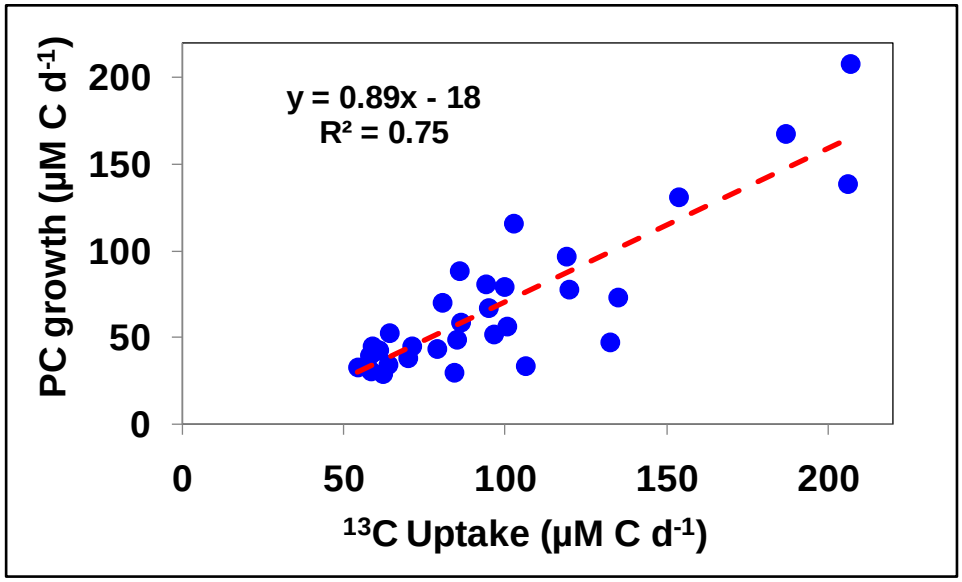

Figure 3.2. Particulate carbon (PC) growth versus calculated carbon uptake measured with ^{13}C. Data from 24 hour incubations at all stations in June and July 2007 and July and August 2008

4. Primary Production Data

Primary production measurements were made along the length of the Murderkill boat sampling transect monthly from April 2007 through December 2008. Information about the incubation experiments and calculations are found in section 3 above.

Data listed in the table:

Station. Eight stations are listed for each sampling date. They are numbered sequentially and represent the DNREC 6-digit station sites.

Station 10 = 206101 – Bowers Beach wharf
Station 11 = 206131 – Webb's Landing
Station 12 = 206141 – Milford Neck
Station 13 = 206711 – 4.45 river mile
Station 14 = 206231 – confluence of Kent County WWTP
Station 15 = 206091 – Bay Road (Rt 1/113)
Station 16 = 206081 – Frederica Rd (Rt 12)
Station 17 = replicate of 206081

DIC = ambient dissolved inorganic carbon concentration as micromoles C L^{-1} (µM C). This parameter measured in our laboratory is needed for calculating the isotopic composition in the calculation of volumetric carbon uptake.

P_{max} = maximum volumetric primary production as micromoles C per liter per day (µM C d^{-1}). The volumetric carbon uptake is calculated for each of the six light levels after the 24-hour incubation by contrasting to the time zero isotopic composition. The P_{max} is the highest carbon uptake of the six light levels; usually at 100% light, occasionally at 60%.

P/B = P_{max} as µg C L^{-1} d^{-1} divided by chlorophyll concentration as µg chlor L^{-1} in units of g/g. The chlorophyll concentration is the ambient chlorophyll for the station measured by the DNREC laboratory.

k = diffuse attenuation coefficient in units of m^{-1}. The k value for each station is calculated from the ambient total suspended sediment (TSS) concentration for that station measured by the DNREC laboratory by dividing TSS/12. The calculation is based on a regression of measured k versus TSS from a series of stations conducted by DNREC in 2007 and 2008 on the Murderkill and is confirmed by a composite regression of k vs TSS from 25 years of sampling by my laboratory along the salinity gradient of the Delaware Estuary (see section 2 above).

APROD = depth-integrated areal primary production in units of mmoles C meter squared per day (mm C m^{-2} d^{-2}). The APROD is calculated using a model that estimates appropriate depths in the water column for the light attenuation value for each of the 6 light levels used in the incubation (100, 60, 35, 15, 7.5, and 1.5% of surface illumination) with extrapolation to 1% light as the theoretical bottom of the photic zone. The light-level simulated depths are derived from the k for that station. The integrated production under a square meter of water surface is derived from a finite solution as a summation of the volumetric production from the six depth intervals.

Explanation of units. Where possible, molar units were used so stoichiometric relationships could be examined. Through extensive aquatic science research over many decades, molar (or atomic) relationships have been described in microbial reactions among the elements carbon, nitrogen, phosphorus, silicon, and oxygen (Redfield et al, 1963). Simple conversion between molar and units of mg L^{-1} can be made with the atomic number of the element. For example, 100 micromolar (µM) C can be converted to 1.2 mg C L-1 by multiplying by 12 (atomic weight of C) and dividing by 1000 (1 mg C = 1000 µg C).

4/24/2007					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1315	52.21	9.11	-6.67	21.66
11	1180	63.72	12.10	-7.83	26.41
12	738	28.93	24.80	-6.58	8.88
13	763	13.45	17.51	-3.92	9.24
14	2182	17.73	25.64	-3.92	8.89
15	545	27.26	27.49	-3.67	17.74
16	527	31.91	26.59	-5.33	15.70
17	538	46.68	39.17	-6.33	17.55

5/30/2007					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1710	69.06	23.74	-3.92	54.88
11	1692	156.46	47.06	-7.58	49.47
12	1568	30.76	22.93	-5.58	14.71
13	1521	59.04	37.29	-4.83	29.72
14	1388	55.68	29.96	-10.25	14.64
15	1017	79.21	28.46	-6.00	36.90
16	944	93.63	35.33	-7.50	38.54
17	960	86.89	33.31	-6.83	33.98

6/26/2007					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1723	106.54	20.89	-1.92	145.84
11	1773	153.77	27.06	-2.33	150.13
12	1865	60.80	29.54	-1.67	77.47
13	1880	86.45	37.86	-1.67	91.61
14	1778	64.29	24.81	-2.58	55.15
15	1623	94.74	34.77	-1.83	108.66
16	1512	85.80	37.44	-1.92	110.59
17	1525	102.76	43.42	-2.08	105.39

7/30/2007					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1795	85.15	30.32	-3.75	43.38
11	1948	118.86	48.85	-2.92	56.79
12	2142	84.07	30.94	-1.75	79.36
13	2148	134.89	45.09	-2.17	82.54
14	2049	100.56	20.52	-3.17	56.20
15	1604	206.10	14.90	-2.92	133.28
16	1579	186.84	12.25	-3.92	135.81
17	1580	207.23	15.64	-5.00	107.25

8/21/2007					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1768	23.58	13.34	-7.75	3.78
11	1924	33.21	19.07	-5.08	6.31
12	2236	15.53	17.92	-2.67	6.28
13	2285	13.65	16.22	-3.08	4.67
14	2612	6.92	10.45	-1.58	5.91
15	2167	14.13	13.78	-2.25	7.39
16	2061	13.16	9.94	-3.33	5.13
17	2057	13.74	10.78	-3.25	3.19

9/25/2007					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1704	37.13	19.54	-3.75	22.29
11	1703	28.91	23.76	-4.50	15.81
12	2312	38.20	27.45	-6.00	12.79
13	2145	55.03	29.22	-6.25	15.33
14	2213	61.79	32.81	-6.50	19.02
15	2244	77.95	20.56	-4.33	35.83
16	2215	84.41	17.96	-3.50	46.16
17	2216	82.46	17.45	-3.08	62.58

10/22/2007					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1876	20.95	22.06	-1.00	53.25
11	1882	15.75	21.03	-1.83	19.80
12	2212	44.00	20.15	-3.92	26.78
13	2176	72.07	29.92	-2.83	45.78
14	2169	53.32	21.91	-4.17	26.79
15	2102	59.97	20.16	-1.58	83.96
16	2078	50.44	21.62	-1.75	67.84
17	2077	50.99	21.17	-1.83	62.04

11/19/2007					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1876	24.93	26.48	-21.42	1.83
11	1870	26.03	15.09	-18.25	2.04
12	1896	7.99	7.92	-12.92	1.36
13	1895	5.46	8.17	-5.00	2.09
14	2023	3.13	4.48	-5.25	1.22
15	1864	6.10	8.16	-4.33	2.42
16	1856	5.32	6.88	-5.92	1.78
17	1855	6.23	8.36	-5.75	1.92

12/19/2007					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1807	10.05	10.05	-6.08	3.36
11	1779	0.41	0.41	-9.17	0.12
12	1683	5.04	9.99	-8.50	1.40
13	1554	1.20	1.56	-6.00	0.54
14	1694	2.74	3.56	-8.58	0.84
15	1362	4.61	5.83	-11.25	0.86
16	1334	4.68	4.72	-16.25	0.66
17	1328	5.35	5.14	-15.33	0.69

1/29/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1695	25.38	8.56	-5.83	9.05
11	1705	32.75	11.42	-7.58	8.19
12	1299	14.03	7.52	-6.33	4.83
13	1674	10.45	9.36	-4.92	4.18
14	2177	2.12	4.08	-2.50	2.09
15	1422	4.89	5.70	-4.67	2.13
16	1305	3.17	4.12	-4.42	1.62
17	1295	3.60	4.38	-4.33	1.61

2/25/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1424	36.40	5.27	-7.08	14.70
11	1381	8.72	3.42	-4.67	5.07
12	1199	4.04	3.52	-3.75	3.16
13	951	7.86	6.50	-4.00	3.72
14	706	10.14	5.69	-3.50	6.58
15	569	17.91	6.53	-2.92	13.49
16	552	15.84	6.67	-3.42	10.56
17	559	16.99	6.64	-3.00	11.61

3/31/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1200	61.46	29.27	-10.92	11.86
11	1211	63.21	32.28	-9.25	11.57
12	1289	26.05	15.10	-4.42	13.29
13	1350	31.51	16.88	-5.67	11.30
14	1524	2.07	1.58	-6.17	0.83
15	1307	22.54	19.32	-3.92	10.87
16	1263	24.70	20.59	-4.42	11.61
17	1271	25.19	19.01	-4.33	11.80

4/21/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1617	94.54	18.24	-16.83	12.96
11	1643	65.68	17.91	-7.00	16.97
12	1632	29.36	13.00	-6.00	10.90
13	1583	33.82	19.99	-5.17	12.84
14	1490	32.22	13.81	-6.75	12.33
15	1260	62.53	19.75	-4.25	31.24
16	1176	60.74	16.27	-4.17	32.86
17	1172	67.64	18.53	-4.42	31.14

5/28/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1673	150.16	59.08	-17.33	22.51
11	1657	77.39	45.52	-5.25	32.37
12	1531	10.83	14.75	-4.42	7.12
13	1469	11.67	15.12	-5.75	4.82
14	2138	73.90	46.68	-4.92	39.05
15	1156	97.65	50.73	-6.25	37.92
16	1005	109.02	37.81	-9.25	34.13
17	1009	128.36	46.96	-8.92	37.19

6/25/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1886	63.36	21.24	-3.58	48.71
11	1964	96.52	37.85	-3.17	68.13
12	2062	90.16	14.74	-5.17	50.61
13	2033	119.65	20.90	-5.92	43.73
14	3200	29.97	25.50	-2.42	33.48
15	1387	100.57	23.66	-4.50	52.18
16	1224	117.78	27.23	-8.75	34.57
17	1234	122.32	29.90	-9.42	30.48

7/7/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	2054	101.70	33.99	-4.42	53.82
11	2133	81.36	40.51	-2.75	71.35
12	2066	45.18	32.27	-1.92	41.43
13	1887	47.83	29.43	-5.83	12.12
14	2612	37.94	33.72	-1.08	63.08
15	1067	114.94	27.31	-6.25	44.34
16	1131	118.75	19.85	-8.00	39.71

7/28/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1975	80.46	35.50	-1.33	151.80
11	1974	59.64	27.96	-1.67	83.14
12	2141	58.00	27.95	-1.33	94.54
13	2156	71.30	27.16	-1.75	82.93
14	2219	62.09	29.33	-3.67	33.51
15	2161	63.64	26.42	-1.33	94.19
16	2169	54.26	22.00	-2.08	56.71
17	2169	58.99	24.00	-2.75	48.46

8/25/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1939	94.01	28.27	-4.50	50.31
11	2005	79.02	21.31	-3.00	64.19
12	2367	58.61	16.83	-2.58	52.68
13	2442	69.79	21.53	-3.67	39.69
14	2956	132.58	30.54	-2.00	209.67
15	2166	96.67	13.03	-3.25	67.07
16	1973	99.81	12.81	-4.75	44.59
17	1993	119.96	14.73	-6.08	46.82

9/25/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1779	93.59	11.46	-34.08	4.62
11	1789	72.30	11.40	-32.92	3.16
12	1990	53.23	9.98	-15.67	4.66
13	2039	73.47	15.63	-10.67	8.90
14	2087	55.66	11.97	-10.42	8.77
15	2205	46.57	17.63	-6.17	13.54
16	2221	48.23	13.71	-6.75	10.40
17	2248	52.53	14.80	-5.00	17.46

10/20/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1978	40.76	33.05	-8.17	10.63
11	2016	29.10	27.28	-5.42	12.59
12	2119	23.12	25.45	-5.50	11.11
13	2147	43.62	40.58	-6.00	11.17
14	2489	12.76	15.65	-2.92	10.19
15	2117	18.41	17.12	-3.75	11.78
16	2099	16.90	17.79	-4.25	10.27
17	2117	20.03	20.19	-4.00	12.74

11/24/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1909	14.86	16.52	-3.75	8.12
11	1910	12.96	13.52	-5.25	5.14
12	1899			-5.58	
13	1904	13.21	15.91	-4.42	5.23
14	1860	3.95	6.12	-6.58	1.29
15	1834	2.70	4.53	-4.42	1.06
16	1832	3.73	5.82	-5.17	1.64
17	1835	3.50	5.68	-5.42	1.40

12/8/2008					
Station	DIC (µM C)	P_{max} (µM C d^{-1})	P/B (g/g)	K (m^{-1})	APROD (mm C $m^{-2}d^{-1}$)
10	1939	17.25	8.85	-12.67	2.19
11	1934	16.07	10.26	-14.08	1.59
12	1817	9.18	10.80	-6.75	2.31
13	1720			-8.67	
14	2513	2.50	6.64	-5.42	1.18
15	1197	4.07	5.95	-8.08	0.97
16	1133	4.90	5.99	-10.00	1.00
17	1057	5.00	6.34	-8.92	1.39

5. Ambient Parameter Data from DNREC

Ambient data for parameters measured by DNREC were used in calculations and in correlations for this report. Data entered by DNREC on the Muderkill Study Group website were extracted and are reported in the tables below in the units measured or were converted to units reported here. The nutrients were converted from the reported units to molar (atomic) units so that stoichiometric evaluations could be made between the nutrient concentrations and carbon parameters.

Data listed in the table:

Station. Eight stations are listed for each sampling date. They are numbered sequentially and represent the DNREC 6-digit station sites.

Station 10 = 206101 – Bowers Beach wharf
Station 11 = 206131 – Webb's Landing
Station 12 = 206141 – Milford Neck
Station 13 = 206711 – 4.45 river mile
Station 14 = 206231 – confluence of Kent County WWTP
Station 15 = 206091 – Bay Road (Rt 1/113)
Station 16 = 206081 – Frederica Rd (Rt 12)
Station 17 = replicate of 206081

Secchi Depth. The disappearance depth of the Secchi Disc was recorded in field notes in tenths of meters. These data were used in an attempt to calculate the bottom of the photic zone (level of 1% of surface light) by multiplying by 3. This is a standard method of estimating the 1% light level that has been well evaluated for the Delaware Estuary (Sharp et al, 2009).

Salinity. Salinity was measured with the hand-held CTD and recorded in field notes. Salinity in units of parts per thousand (‰) was used in some plots as an indicator of flow conditions.

Total Suspended Sediments (TSS). TSS was measured in the DNREC laboratory by the accepted EPA method and recorded in units of milligrams per liter (mg L^{-1}). As a better indicator of light attenuation than the Secchi depth, the TSS was used to calculate the diffuse attenuation coefficient (see section 3 above).

Chlorophyll. The chlorophyll concentration was measured in the DNREC laboratory by filtering samples, extracting in acetone, and reading on filter fluorometer by accepted EPA method. Chlorophyll was recorded in units of micrograms per liter (µg L^{-1}).

Nutrients. The nutrients **nitrate plus nitrite (N&N)**, **ammonium (NH_4)**, **phosphate (PO_4)**, and **silicate (Si)** were measured in sample filtrates in the DNREC laboratory using an autoanalyzer with EPA approved methods. Nutrients were recorded in units of milligrams per liter of the element (mg N L^{-1}, mg P L^{-1}, mg Si L^{-1}). For the tables below and for calculating stoichiometric relationships, nutrients were converted to molar units, converting from milligrams to micrograms by multiplying by 1000 and then dividing by the atomic weight of the element. The formulae used are:

µM N = ((mg N L^{-1})*1000)/14

µM P = ((mg P L^{-1})*1000)/31

µM Si = ((mg Si L^{-1})*1000)/28

It has been discovered recently that since sometime in 2007, the DNREC laboratory analysis for ammonium in saline samples gave erroneously high concentration values. As a result, all ammonium concentrations for samples with salinity exceeding 7 ‰ are highlighted in red in the following charts and are considered suspect (too high).

Dissolved Oxygen (**DO**) was measured in samples fixed in the field and returned to the DNREC laboratory for Winkler titration. DO concentration was reported as mg L^{-1}. For the tables below and for calculating stoichiometric relationships, DO concentrations were converted to molar units, converting from mg O_2 L^{-1} to micrograms by multiplying by 1000 and then dividing by the atomic weight of oxygen (16).

04/24/2007									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.3	18.24	80	68.8	1.57	17.86	0.13	71.43	723
11	0.25	14.21	94	63.2	33.07	11.21	0.23	85.71	620
12	0.25	0.62	79	14.0	160.00	13.36	2.00	289.29	421
13	0.3	0.42	47	9.2	174.29	12.93	2.61	303.57	419
14	0.4	0.42	47	8.3	228.57	20.14	19.35	417.86	423
15	0.35	0.15	44	11.9	217.14	13.86	1.71	278.57	470
16	0.3	0.13	64	14.4	220.71	11.50	1.52	307.14	468
17	0.3	0.13	76	14.3	237.86	10.79	1.48	260.71	468

05/30/2007									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.4	23.37	47	34.9	1.00	11.00	0.23	25.00	453
11	0.3	21.72	91	39.9	7.57	10.86	0.45	50.00	391
12	0.5	6.79	67	16.1	108.57	14.29	5.32	303.57	230
13	0.3	3.75	58	19.0	126.43	14.79	7.03	267.86	221
14	0.3	1.59	123	22.3	185.71	12.79	6.90	246.43	270
15	0.2	0.47	72	33.4	179.29	8.71	3.10	317.86	341
16	0.2	0.33	90	31.8	186.43	9.86	1.84	114.29	368
17	0.2	0.33	82	31.3	187.14	9.21	2.13	117.86	363

06/26/2007									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.4	18.93	23	61.2	0.57	10.36	0.35	100.00	434
11	0.5	19.07	28	68.2	0.36	10.14	0.61	96.43	377
12	0.6	6.67	20	24.7	37.36	13.00	2.61	325.00	246
13	0.5	6.36	20	27.4	37.57	15.43	2.97	360.71	206
14	0.4	3.41	31	31.1	54.43	13.00	3.10	382.14	233
15	0.4	2.45	22	32.7	64.64	34.36	2.77	342.86	271
16	0.4	1.97	23	27.5	69.79	8.57	2.52	382.14	288
17	0.4	1.97	25	28.4	75.00	11.71	2.55	367.86	288

07/30/2007									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.4	25.11	45	33.7	2.36	29.86	1.52	64.29	244
11	0.6	20.19	35	29.2	8.57	29.14	5.90	167.86	184
12	0.7	13.94	21	32.6	13.43	20.93	9.61	267.86	158
13	0.6	10.99	26	35.9	17.93	17.29	10.42	335.71	151
14	0.5	7.98	38	58.8	21.07	16.29	9.06	350.00	191
15	0.4	3.65	35	166.0	13.21	6.29	3.58	214.29	379
16	0.4	3.22	47	183.0	12.43	6.64	2.97	164.29	344
17	0.4	3.22	60	159.0	12.86	10.14	3.39	167.86	344

08/21/2007									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.1	21.39	93	21.2	10.64	16.43	2.29	78.57	324
11	0.1	21.64	61	20.9	8.64	19.29	3.55	96.43	296
12	0.3	16.09	32	10.4	21.29	20.71	8.97	282.14	227
13	0.5	13.10	37	10.1	27.57	20.71	13.84	325.00	197
14	0.5	5.40	19	7.9	102.86	26.43	57.74	685.71	222
15	0.7	8.23	27	12.3	32.57	21.43	13.52	364.29	215
16	0.7	7.07	40	15.9	30.79	24.29	11.65	292.86	244
17	0.7	7.07	39	15.3	28.21	25.00	11.58	296.43	244

09/25/2007									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.6	24.56	45	22.8	0.50	37.86	0.84	42.86	455
11	0.7	24.56	54	14.6	0.93	4.79	1.00	32.14	446
12	0.5	20.03	72	16.7	9.50	10.00	3.84	78.57	349
13	0.6	15.36	75	22.6	19.07	10.71	6.26	89.29	317
14	0.5	11.95	78	22.6	24.79	7.14	7.45	107.14	304
15	0.5	7.72	52	45.5	32.36	5.79	8.81	146.43	346
16	0.4	6.55	42	56.4	34.29	5.14	8.77	171.43	376
17	0.4	6.55	37	56.7	33.93	4.93	8.90	171.43	368

10/22/2007									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	1.1	21.18	12	11.4	0.86	2.14	1.32	117.86	501
11	1.2	24.17	22	9.0	1.50	2.14	1.52	135.71	487
12	0.8	9.62	47	26.2	32.00	9.29	10.45	417.86	343
13	0.7	12.06	34	28.9	25.57	10.00	9.10	382.14	355
14	0.6	6.12	50	29.2	40.64	10.00	11.74	492.86	314
15	0.8	5.57	19	35.7	40.57	9.29	11.32	507.14	336
16	0.8	4.91	21	28.0	38.93	12.86	11.58	525.00	319
17	0.8	4.91	22	28.9	37.71	11.43	10.90	525.00	320

11/19/2007									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.2	24.57	257	11.3	27.57	63.21	1.29	103.57	650
11	0.1	24.72	219	20.7	27.36	70.79	1.55	135.71	650
12	0.2	21.68	155	12.1	35.79	49.14	3.00	171.43	618
13	0.3	15.65	60	8.0	64.71	34.21	6.65	300.00	591
14	0.4	6.44	63	8.4	138.57	14.86	18.84	582.14	556
15	0.4	9.64	52	9.0	91.43	18.07	8.48	453.57	579
16	0.4	8.54	71	9.3	100.00	16.64	8.87	482.14	569
17	0.4	8.54	69	8.9	97.14	17.50	8.84	478.57	569

12/19/2007									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.3	21.36	73	12.0	41.64	63.86	1.29	107.14	694
11	0.4	20.84	110	12.2	45.50	52.14	1.16	153.57	698
12	0.4	15.70	102	6.1	70.21	38.43	1.81	246.43	693
13	0.5	8.23	72	9.2	107.86	21.21	2.45	421.43	661
14	0.5	1.87	103	9.2	160.00	21.36	3.81	710.71	602
15	0.4	2.51	135	9.5	146.43	22.64	2.97	653.57	608
16	0.4	1.74	195	11.9	151.43	22.50	3.10	639.29	614
17	0.4	1.74	184	12.5	151.43	22.57	3.06	642.86	615

01/29/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.2	19.61	70	35.6	44.86	32.36	0.68	107.14	789
11	0.3	18.75	91	34.4	50.07	42.07	1.13	150.00	776
12	0.3	12.64	76	22.4	100.71	21.86	2.74	328.57	739
13	0.4	9.59	59	13.4	124.29	26.21	3.35	421.43	727
14	0.5	4.07	30	6.2	152.86	16.71	5.71	703.57	647
15	0.3	4.33	56	10.3	175.00	20.36	3.74	567.86	723
16	0.3	3.28	53	9.2	187.14	21.86	3.55	578.57	714
17	0.3	3.28	52	9.9	179.29	21.21	3.61	575.00	714

02/25/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.2	10.41	85	82.8	90.00	13.21	0.77	253.57	732
11	0.4	4.77	56	30.6	149.29	13.57	2.55	496.43	666
12	0.4	1.73	45	13.8	194.29	11.79	3.39	571.43	643
13	0.5	0.77	48	14.5	222.86	9.29	2.65	603.57	639
14	0.4	0.38	42	21.4	246.43	7.14	1.68	589.29	684
15	0.3	0.20	35	32.9	260.71	3.57	1.10	575.00	724
16	0.3	0.19	41	28.5	225.00	5.50	1.16	546.43	724
17	0.3	0.19	36	30.7	227.86	5.50	1.16	535.71	724

03/31/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.1	8.70	131	25.2	49.43	18.93	0.42	107.14	660
11	0.2	8.60	111	23.5	52.79	19.86	0.48	110.71	658
12	0.4	6.35	53	20.7	82.86	15.36	1.23	217.86	619
13	0.5	3.26	68	22.4	135.00	15.64	2.19	385.71	559
14	0.3	0.81	74	15.7	180.00	14.79	3.52	550.00	512
15	0.4	0.92	47	14.0	176.43	14.00	2.90	517.86	519
16	0.4	0.71	53	14.4	183.57	12.21	2.84	525.00	539
17	0.4	0.71	52	15.9	182.86	12.71	2.84	510.71	541

04/21/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.1	20.99	202	62.2	9.71	52.93	0.26	64.29	559
11	0.3	18.07	84	44.0	13.36	35.14	0.65	110.71	488
12	0.4	10.12	72	27.1	35.36	18.93	1.48	164.29	432
13	0.5	7.47	62	20.3	44.71	13.21	1.77	171.43	435
14	0.3	4.62	81	28.0	60.21	9.57	2.06	200.00	408
15	0.4	1.90	51	38.0	81.43	5.36	1.45	175.00	478
16	0.4	1.57	50	44.8	88.57	3.86	1.13	128.57	499
17	0.4	1.57	53	43.8	85.00	3.93	1.19	150.00	499

05/28/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.1	22.16	208	30.5	2.07	41.93	0.48	10.71	449
11	0.3	19.34	63	20.4	11.00	31.07	1.26	103.57	458
12	0.5	8.15	53	8.81	64.71	19.07	5.23	332.14	371
13	0.6	4.32	69	9.26	86.43	17.64	9.26	371.43	337
14	0.5	0.73	59	19.0	167.14	15.79	16.45	657.14	384
15	0.4	0.93	75	23.1	115.71	12.00	8.55	375.00	428
16	0.3	0.63	111	34.6	125.71	10.57	5.61	321.43	478
17	0.3	0.63	107	32.8	117.86	7.79	5.94	296.43	478

06/25/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.4	23.60	43	35.8	3.86	60.43	0.94	75.00	350
11	0.5	20.39	38	30.6	7.93	47.57	2.06	164.29	333
12	0.3	8.65	62	73.4	29.50	7.86	5.19	332.14	310
13	0.4	6.41	71	68.7	38.43	5.71	5.42	378.57	309
14	0.5	1.67	29	14.1	82.86	23.86	12.32	867.86	216
15	0.3	1.40	54	51.0	73.57	9.64	3.16	250.00	313
16	0.3	0.97	105	51.9	77.86	9.79	2.13	175.00	315
17	0.3	0.97	113	49.1	78.57	10.57	2.13	160.71	316

07/07/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.5	24.70	53	35.9	4.00	82.14	2.45		294
11	0.6	19.22	33	24.1	10.00	53.79	3.94		191
12	0.4	10.67	23	16.8	18.57	26.64	5.61		138
13	0.4	7.25	70	19.5	27.43	19.43	5.19		144
14	0.5	3.11	13	13.5	63.64	26.79	34.19		166
15	0.3	0.92	75	50.5	55.71	14.21	1.84		286
16	0.3	1.19	96	71.8	43.07	12.79	2.03		284

07/28/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.5	27.65	16	27.2	0.57	68.36	2.06	60.71	345
11	0.6	27.74	20	25.6	0.79	81.43	2.03	64.29	349
12	0.6	19.69	16	24.9	7.93	45.79	5.68	203.57	284
13	0.4	16.60	21	31.5	8.86	42.57	6.61	250.00	253
14	0.2	10.12	44	25.4	14.00	21.57	7.61	353.57	182
15	0.3	9.56	16	28.9	16.57	16.43	7.87	350.00	216
16	0.3	8.91	25	29.6	18.29	17.57	7.87	335.71	168
17	0.3	8.91	33	29.5	17.07	16.36	8.16	314.29	169

08/25/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.2	27.95	54	39.9	0.79	106.43	1.77	60.71	433
11	0.3	26.72	36	44.5	0.50	117.14	2.84	114.29	399
12	0.5	18.62	31	41.8	8.36	54.79	7.19	246.43	316
13	0.6	15.48	44	38.9	13.50	41.86	9.03	292.86	289
14	0.4	6.90	24	52.1	64.93	16.36	32.58	642.86	283
15	0.4	8.00	39	89.0	16.64	8.14	7.03	285.71	352
16	0.4	6.65	57	93.5	16.29	6.07	5.55	253.57	376
17	0.4	6.65	73	97.7	18.36	6.07	5.81	253.57	377

09/25/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.1	25.85	409	98.0	9.14	82.86	3.00	78.57	436
11	0.1	25.56	395	76.1	10.43	80.71	1.29	71.43	435
12	0.2	27.34	188	64.0	5.86	68.79	1.97	103.57	410
13	0.2	27.30	128	56.4	6.57	70.57	2.10	92.86	384
14	0.2	26.45	125	55.8	9.14	64.00	2.71	110.71	373
15	0.3	23.59	74	31.7	23.71	70.64	4.23	175.00	368
16	0.3	22.82	81	42.2	26.93	73.57	4.48	185.71	339
17	0.3	22.81	60	42.6	26.93	84.29	4.45	182.14	339

10/20/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.1	24.43	98	14.8	18.07	67.64	1.77	142.86	458
11	0.1	24.17	65	12.8	19.93	71.43	2.32	185.71	438
12	0.2	22.31	66	10.9	38.50	52.79	3.45	207.14	392
13	0.3	21.36	72	12.9	48.36	57.14	4.35	232.14	373
14	0.5	14.79	35	9.78	266.43	33.79	17.03	475.00	375
15	0.4	18.37	45	12.9	40.29	47.64	3.84	257.14	351
16	0.4	17.3	51	11.4	41.64	47.21	3.94	257.14	361
17	0.4	17.3	48	11.9	41.71	37.00	4.45	253.57	359

11/24/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.3	25.82	45	10.8	23.71	108.57	0.68	110.71	388
11	0.3	25.45	63	11.5	15.79	92.86	0.77	125.00	408
12	0.2	14.92	67	9.99	44.07	73.57	1.74	260.71	433
13	0.4	15.29	53	9.96	60.21	72.14	2.35	357.14	473
14	0.2	6.63	79	7.74	100.71	48.43	3.42	596.43	561
15	0.3	5.39	53	7.16	110.71	47.36	3.48	650.00	579
16	0.3	4.7	62	7.69	113.57	49.14	3.58	660.71	621
17	0.3	4.7	65	7.4	115.71	49.43	3.58	667.86	619

12/08/2008									
Station	Secchi	Salinity	TSS	Chlor	N&N	NH_4	PO_4	Si	DO
	(m)	(‰)	(mg L^{-1})	(µg L^{-1})	(µM N)	(µM N)	(µM P)	(µM Si)	(µg-at L^{-1})
10	0.1	22.98	152	23.4	33.86	70.71	0.74	71.43	718
11	0.1	19.13	169	18.8	54.29	75.00	1.19	225.00	730
12	0.2	6.25	81	10.2	145.00	63.93	2.65	407.14	638
13	0.2	3.37	104	6.08	166.43	72.14	3.16	489.29	606
14	0.2	0.82	65	4.52	314.29	50.00	4.94	746.43	559
15	0.1	0.79	97	8.21	208.57	39.57	2.74	546.43	603
16	0.1	0.64	120	9.81	216.43	33.50	2.65	742.86	612
17	0.1	0.64	107	9.47	215.71	35.43	2.74	725.00	613

6. Correlations of Primary Production with Ambient Conditions

The boat sampling transect along the Murderkill River was designed partially to assess influences on primary production from nutrient inputs from the Kent County WWTF. The primary production data from this study are given in section 4 and appropriate ambient parameter data from DNREC are given in section 5. In this section, these data are analyzed to evaluate influences on primary production. The subject of nutrient fluxes within the Murderkill River watershed is addressed in other projects in the Murderkill Study Group. In discussing the patterns of primary production and influence of nutrients, I first examine nutrient profiles along the river sampling runs and then evaluate primary production data.

Wastewater treatment effluents are not usually considered sources of elevated silicate. As a soil leachate, silicate was expected to be higher upstream with dilution going toward station 10 at the juncture with the Delaware Bay. On a number of occasions, there was elevation of silicate near the confluence of the WWTF discharge ditch (station 14). On 10 of the 22 sampling dates, the silicate concentration at station 14 was appreciably higher than at adjacent stations. Four examples of silicate concentrations along the riverine transect are shown in Figure 6.1 to emphasize the differences in pattern. In the November and September examples, there is high or moderate silicate upstream with dilution along the salinity gradient. The August profile shows large elevation at station 14 and the July example shows slight elevation in this vicinity, but elevation also at stations 13 and 12.

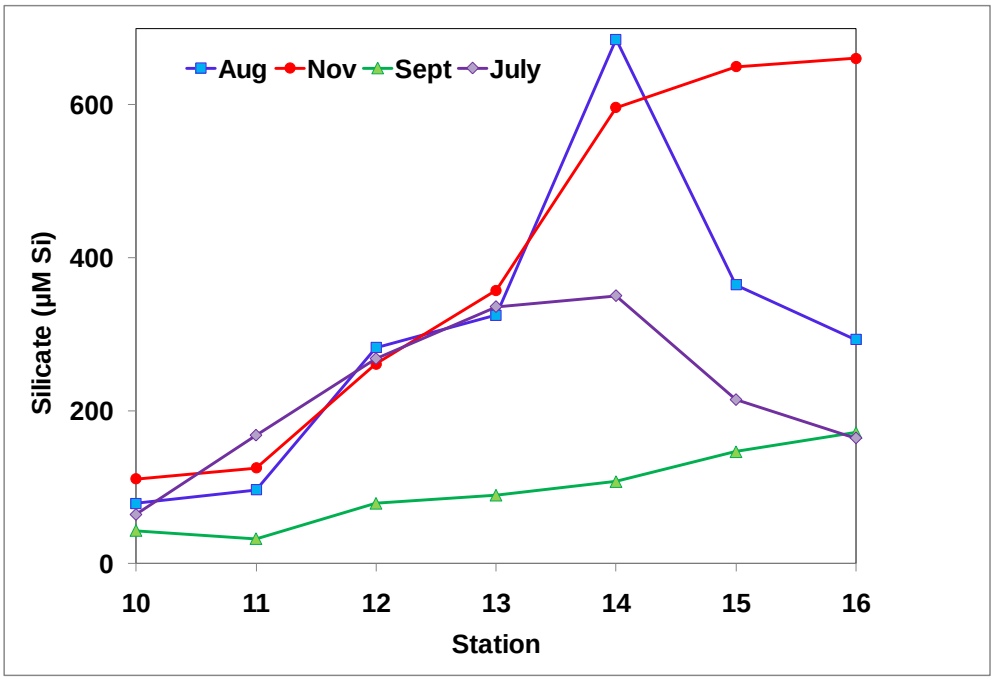

Figure 6.1. Four examples of silicate distribution along the sampling gradient of the Murderkill River.

Both wastewater treatment plants and agricultural fertilization are expected sources of phosphate. Therefore, dilution going from upstream to downstream with elevation near station 14 would be an expected pattern. This was seen on almost all of the sampling dates. The average phosphate concentration for the 22 samplings at the upstream station (16) was 4.51 µM P; at the downstream station (10), it was 0.92 µM P and at station 14, it was 12.83 µM P. Large dilution of upstream concentrations were seen in all cases in the transect down the salinity gradient to the confluence with the Delaware Bay (Figure 6.2). Also, a very large phosphate input was seen from the WWTF. The August example is typical of many of the sampling dates; a very large elevation at station 14. The May example is typical of input, but a comparatively smaller elevation at station 14. The July and February transects are rarer examples; they show dilution of an upstream elevation going down the salinity gradient without noticeable input from station 14.

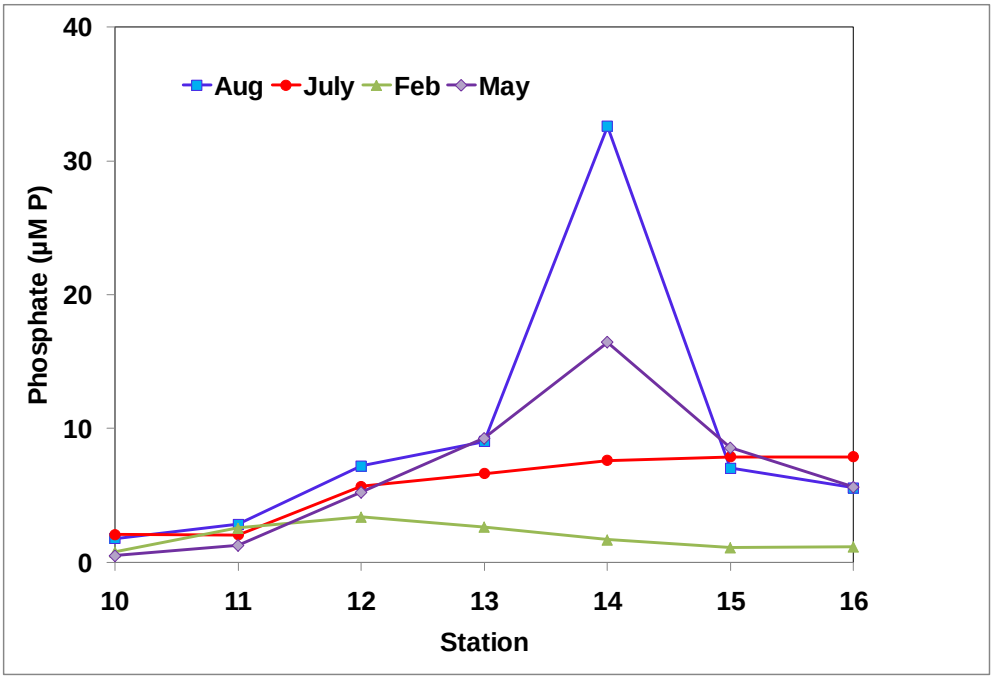

Figure 6.2. Four examples of phosphate distribution along the sampling gradient of the Murderkill River.

Nitrate, like phosphate, should have a pattern of dilution from watershed agricultural inputs and wastewater effluent inputs; the wastewater inputs can occur at the effluent location as nitrate formed in the treatment plant or as elevation downstream from nitrification within the receiving waters. The direct input is the pattern seen from the river transects (Figure 6.3). The average upstream station 16 concentration was 100 µM N; the average station 10 concentration was 17 µM N; and the average station 14 concentration was 122 µM N. The elevation at station 14 was considerably less extreme than that for phosphate. The October profile shown is unique with a very large elevation at station 14. Otherwise the elevation was less than 50%, and often only a small percentage elevation over the adjacent stations; the December profile is more typical. The February example, with high concentration upstream and the July one with low upstream concentration are examples that show no elevation at station 14.

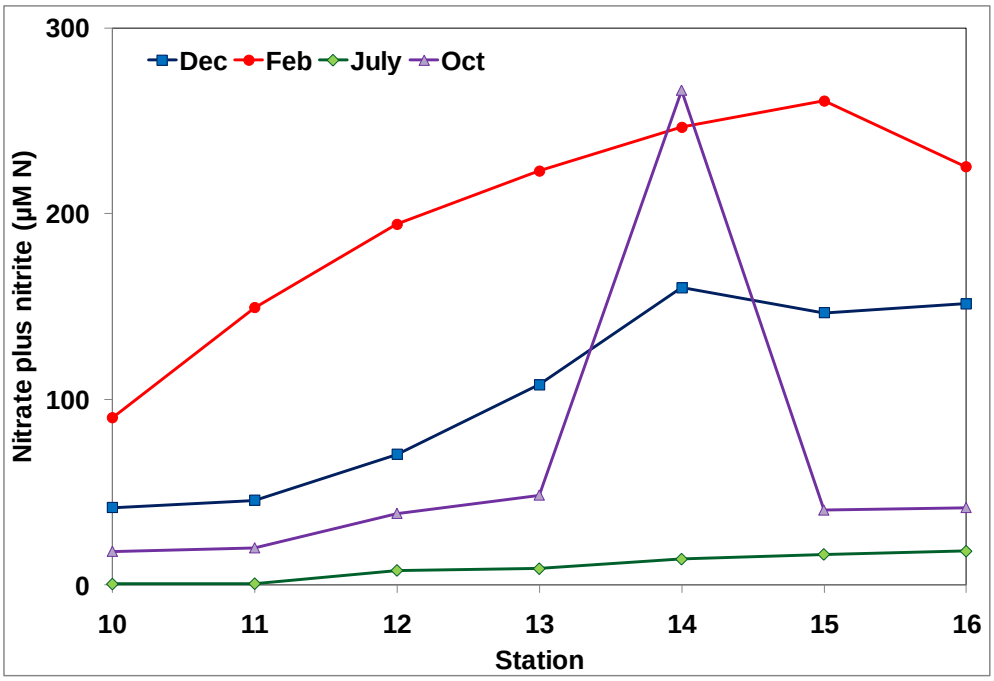

Figure 6.3. Four examples of distribution of nitrate plus nitrite along the sampling gradient of the Murderkill River.

There is less of an expected pattern for ammonium. The average concentration at station 16 was 19.2 µM N; at station 10, it was 48.1 µM N; at station 14, it was 22.3 µM N. A direct input from a wastewater facility with minimal treatment would have a high ammonium content. In this case, the ditch is relatively distant from the WWTF, giving ample time for oxidation of ammonium to nitrate. Considerable ammonium input from the marshes along the river is also expected. In examples of ammonium profiles, rarely, like in the June example, a slight elevation was seen near station 14 (Figure 6.4). A more common pattern was of a steady increase going downstream as in the November and December profiles, with highest concentration at the bay end. Another pattern is a relatively uniform concentration along the gradient, as in the August sampling. It would appear that a major source of ammonium for the Murderkill River is diffuse marsh input. However, the very high concentrations at the highest salinity station is puzzling. Recent discussion with DNREC laboratory personnel indicates that there is an analytical problem in the laboratory with saline samples giving ammonium values that are artificially too high. Thus, the best conclusion that can be made for the ammonium distribution is that in going downstream from station 16 to station 13, there is almost never indication of input from station 14. For the higher salinity samples at stations 12, 11, and 10, the reported concentrations are suspect (see tables in section 5).

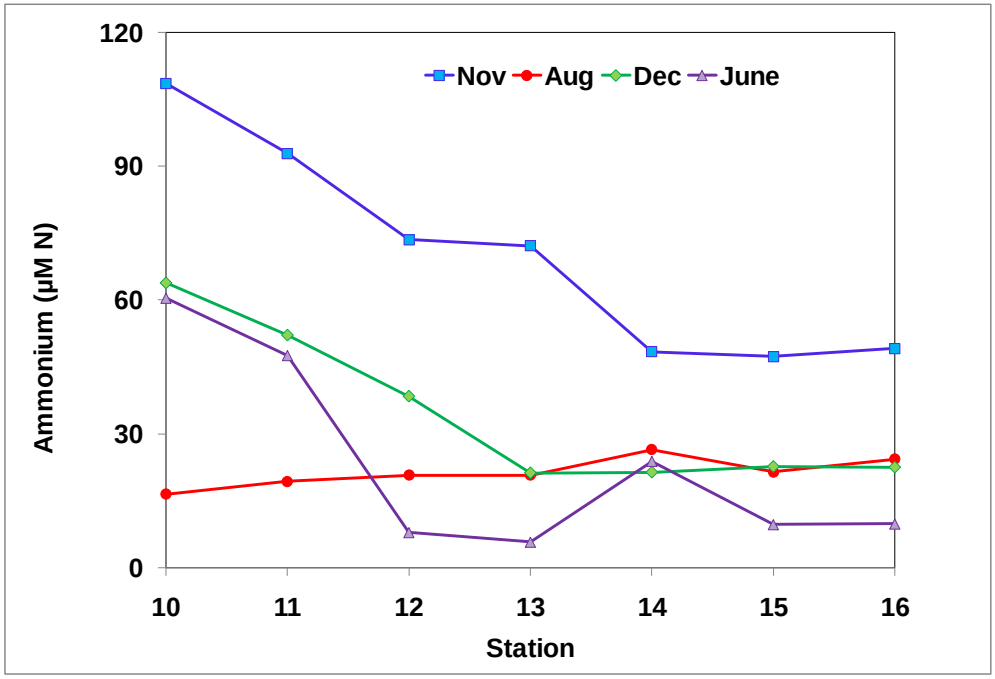

Figure 6.4. Four examples of ammonium distribution along the sampling gradient of the Murderkill River. Values for stations 12, 11, and 10 are suspect of being artificially high due to analytical error with saline samples.

The plot of TSS along the sampling gradient can be examined to evaluate if total suspended sediment loading from the wastewater treatment plant was important. The average TSS concentration at upstream station 16 was 62 mg L^{-1}; at station 10, the average was 97 mg L^{-1}; at station 10, the average concentration was 70 mg L^{-1}. There is little evidence of TSS loading from the wastewater facility. Representative plots of TSS at each station are shown In Figure 6.5. The May plot shows elevation at station 14, a relatively rare occurrence. In the December plot, the highest concentrations are found upstream with dilution going toward the bay. In the November example, the opposite is the case with highest concentrations at the station closest to the bay. In the June example, TSS concentrations were relatively low and uniform along the sampling gradient. Since the river is shallow and muddy, resuspension from tidal currents is probably the major control of TSS concentrations. As a result the distribution of TSS is largely determined by the tidal cycle at the time of sampling.

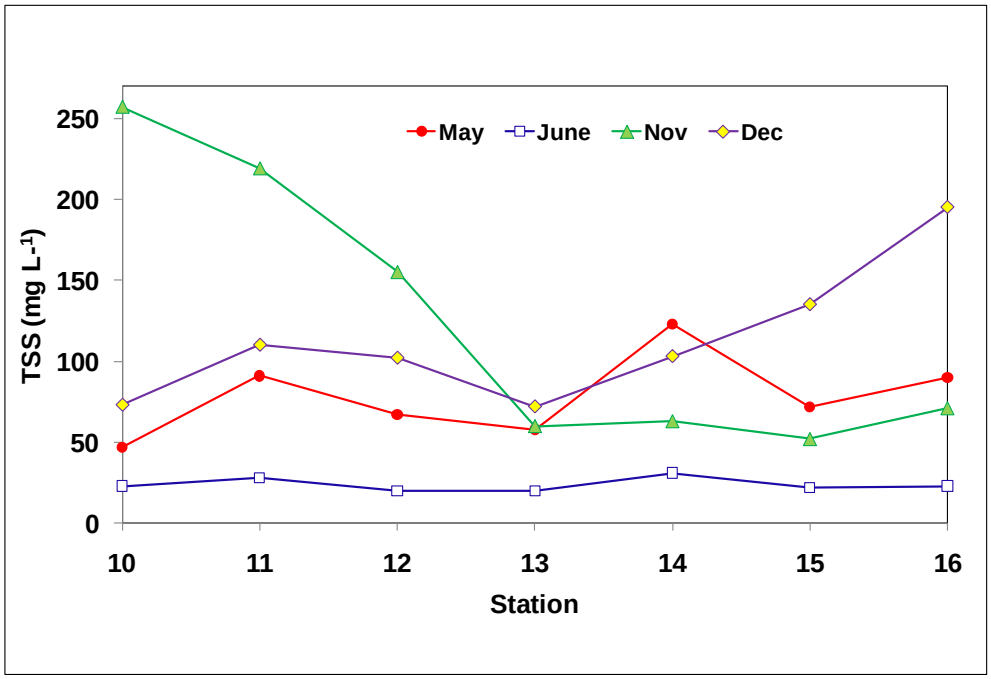

Figure 6.5. Four examples of distribution of total suspended sediments (TSS) along the sampling gradient of the Murderkill River.

Overall, it appears that the wastewater effluent ditch was a major source of phosphate, a proportionately less large source of nitrate, and not a source of ammonium nor of TSS. It also appears that the ditch was a relatively large source of silicate, which is a less expected outcome.

Since we regularly measured the dissolved inorganic carbon (DIC) concentration of all the samples, we can also evaluate the influence of the wastewater facility for this parameter. As a major seawater component, DIC should be highest at the saltwater end of an estuarine gradient and have a freshwater concentration dependent upon the watershed input. In highly alkaline soils, the freshwater DIC concentration can be high and some estuaries with limestone watersheds, such as in west Texas, have higher concentrations in freshwater than in seawater. Usually, large estuaries in the mid-Atlantic region do not have high limestone content of the watersheds and show an increasing DIC with salinity. The DIC distribution observed along the sampling transect was somewhat unexpected. From all of the samplings, the average DIC at station 10 was 1756 µM C; close to what would be expected at the average salinity at this station. The average DIC at station 16 was 2094 µM C; more than double what would be expected at that salinity. The average DIC at station 14 was 1821 µM C. In the representative plots shown (Figure 6.6), the May pattern had elevated concentration at upstream station 16, but the expected increase going toward the Delaware Bay. The April plot showed a somewhat similar pattern; however, there was a large elevation at station 14. The August plot showed high DIC at the upstream end with lower at the bay end. The November plot was almost flat along the transect. It would appear that the small volume of river water is overwhelmed with watershed inputs, probably indicating respiratory CO_2 from marsh outwelling . While many of the samplings show DIC concentration at station 14 that is higher than the saltwater endmember of the transect, the concentration there was often close to that of adjacent stations; like that in the August plot.

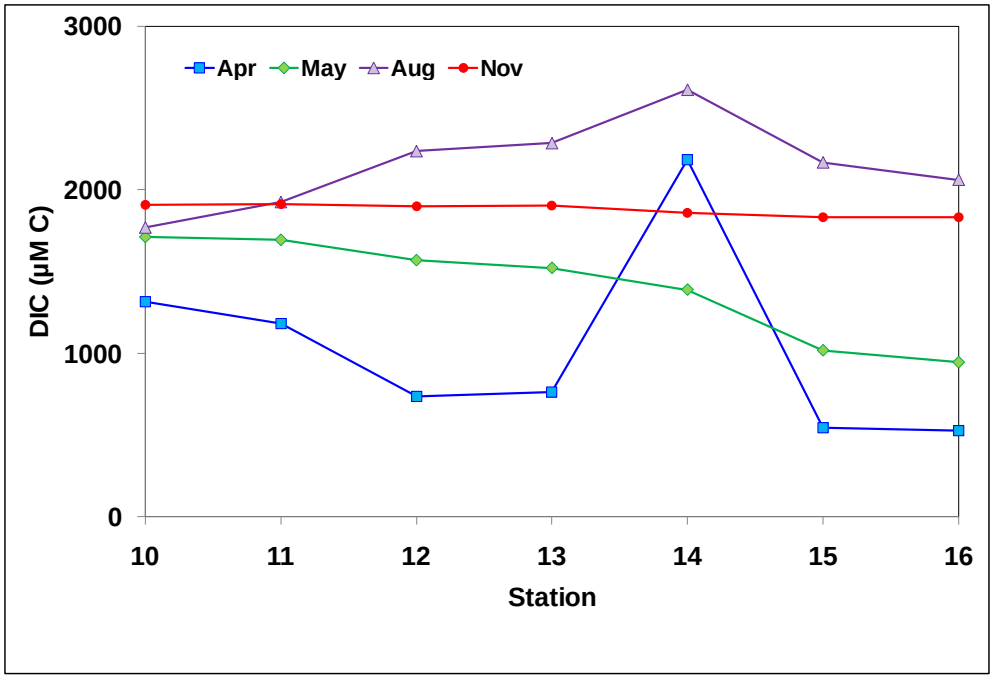

Figure 6.6. Four examples of distribution of dissolved inorganic carbon (DIC) along the sampling transect of the Murderkill River.

By plotting the concentration of a chemical parameter against salinity, apparent biogeochemical behavior can be illustrated. This approach, pioneered by the Dutch, was used extensively in the past (Liss, 1976) and has been illustrated as an effective tool in the Delaware Estuary (Sharp et al, 1982). The concept is that a parameter with a dominant freshwater input will dilute along a salinity gradient to a low oceanic end concentration. As an opposite trend, a constituent that is primarily of seawater origin will increase along a salinity gradient from a low freshwater endmember concentration. Silicate should primarily have a watershed input with dilution along the salinity gradient of the river. By plotting silicate versus salinity, it is possible to evaluate this type of distribution (Figure 6.7). The upstream station 16 was closest to zero salinity and the high salinity always was found at station 10, near the confluence of the Murderkill River with the Delaware Bay. The plot of silicate vs salinity showed a dilution with salinity and the regression line had a negative slope and a regression coefficient of 0.45. The data points highlighted as blue squares were from station 14 when that station had a considerably higher silicate than any other station. If the regression coefficient is interpreted as showing that 45% of the scatter of the data was due to dilution of the zero salinity input, then part of the deviation from it being higher was due to the elevated silicate from the effluent of the wastewater treatment canal. The remainder of the scatter was due to the variability, probably from multiple inputs along the river.

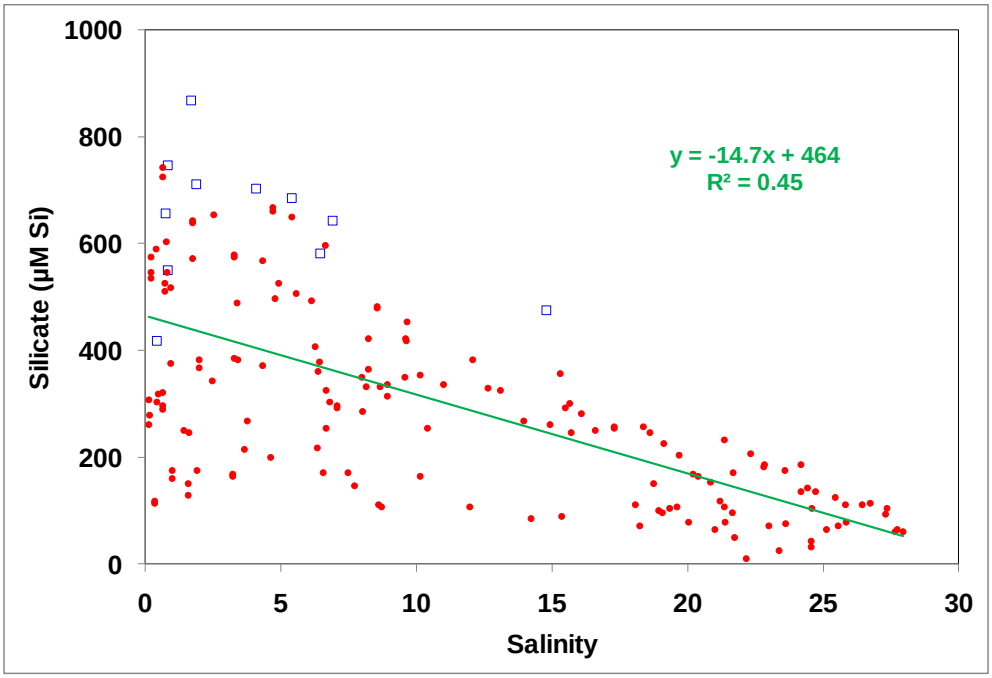

Figure 6.7. The concentration of silicate versus salinity for all samples taken from the Murderkill River transect Data points highlighted as empty blue squares were from station 14 at times when that station had the highest silicate concentration along the sampling transect.

The expectation is that DIC plotted against salinity should show a positive correlation, increasing from a low freshwater concentration to a higher one at the seawater end of the gradient. A plot is shown of all the DIC versus salinity data for the 8 stations from the 21 sampling dates (Figure 6.8). The dashed green line on the plot is a regression based on hundreds of measurements from the Delaware River and Bay Estuary and adjacent coastal waters; the equation is DIC = 36 (salinity) + 815 (Sharp et al, 2009). The plot of Murderkill River data showed that the zero salinity and highest salinity ends were fairly close to the expected linear dilution line for the Delaware Estuary, but that there was considerable scatter from inputs along the salinity gradient. A regression of the data gave a regression coefficient of 0.21, indicating that close to 80% of the scatter was from outside the dilution line. Data outlined as blue squares were from station 14; some of the most extreme outliers were from the wastewater treatment effluent canal. This might indicate respiratory CO_2 input from the wastewater stream. If all of the station 14 data are removed the regression of DIC vs salinity for the other stations had a coefficient of 0.37, indicating that more than 60% of the scatter still was from diffuse inputs along the transect. This may be a combination of high respiratory CO_2 from marsh runoff and possibly also agricultural runoff influenced by lime addition to soils.

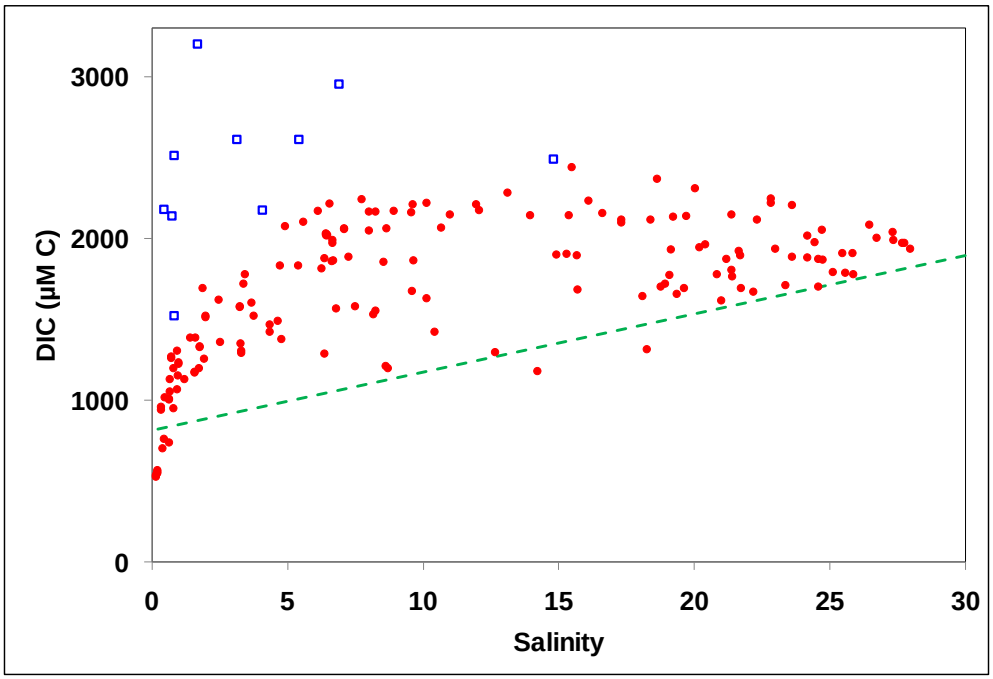

Figure 6.8. The concentration of dissolved inorganic carbon (DIC) versus salinity for all samples taken from the Murderkill River transect Data points highlighted as empty blue squares were from station 14 at times when that station had the highest DIC concentration along the sampling transect.

Primary production measurements were made monthly from April 2007 through December 2008. The maximum volumetric production (P_{max}) is the highest production for an individual bottle from the incubation light series. An individual sample was divided into a series of bottles that were incubated for 24-hours at 100% light and a series of attenuation levels to 1.5% of ambient light. Usually the bottle with 100% light was the P_{max}; the 60% light level was slightly higher than the 100% level in about 15% of the incubations. The P_{max} values are shown for all 7 stations and all 21 samplings in Figure 6.9.

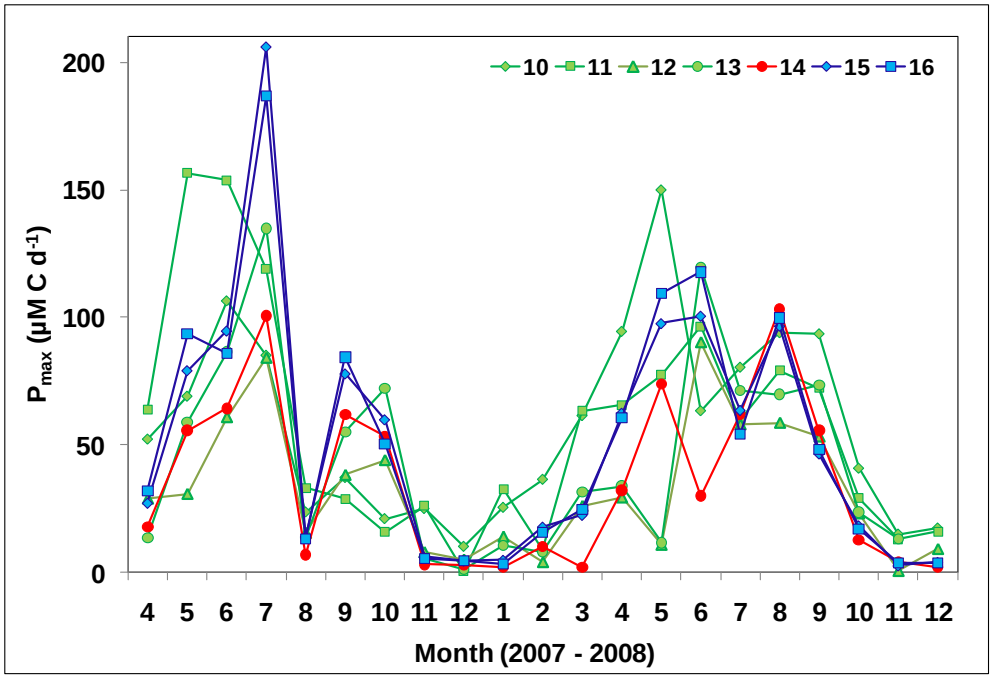

Figure 6.9. Maximum primary production (P_{max}) for all seven stations at each sampling time from April 2007 through December 2008. Stations upstream (15 and 16) of the wastewater treatment canal have blue symbols and lines; the wastewater treatment canal (station 14) is in red; stations downstream of the canal (13, 12, 11, 10) are in green.

These plots show expected low production in the winter and higher in the summer. They do not show noticeable elevation of production at station 14. It is obvious that August 2007 had anomalously low production at all stations. This was due to the incubation being done on an overcast day with little sunlight. August 2008 had high production at most stations. Also, July 2008 production was low at most stations, while July 2007 was higher; extremely high at stations 15 and 16. The 21 monthly samplings allows for average monthly values for the 4th through 12th months and single 2008 values for January – March.

Plots are shown for monthly averages for station 16 as the most upstream station, station 10 as the highest salinity station at the confluence of the river with the Delaware Bay, and station 14 at the junction with the wastewater treatment plant effluent canal (Figure 6.10). In the plot of P_{max}, production was low in November – March and highest in May-September. Even with the averaging, the annual curve is not smooth and the August values still were a bit low. Production at station 10 appears to consistently be higher than at station 16 for most of the year and both the upstream and downstream stations are higher than station 14 most of the time.

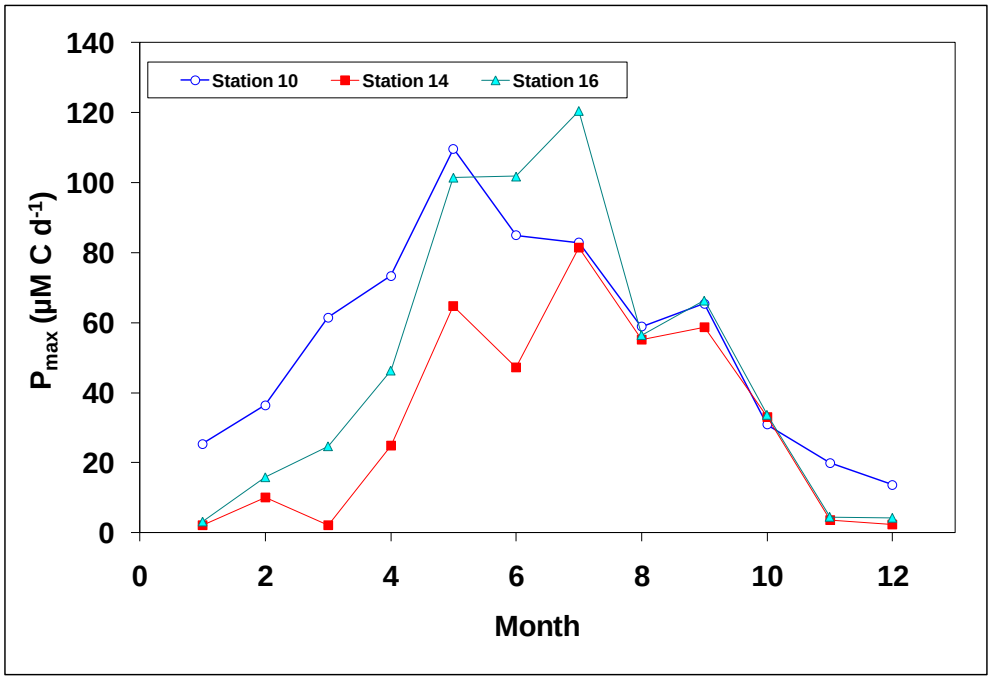

Figure 6.10. Average monthly maximum primary production (P_{max}) for the most upstream station 16, wastewater treatment canal station 14, and most downstream station 10. January, February, and March values are based on single 2008 sampling; all other months are average values from 2007 and 2008 sampling.

In environments with variation in light penetration, calculation of depth-averaged areal production can be more informative than P_{max} measurements. As was discussed in section 2, diffuse light attenuation coefficients (k) were calculated from measured TSS values. Many of the k values were large, giving a 1% light level less than 1 m deep; about one third of the k values gave 1% light levels deeper than 1 m, but almost none deeper than 2 m. Because of the extreme light attenuation of this turbid estuarine river, estimates of areal primary production are less robust than would be the case with clearer waters. As Figure 6.11 shows, calculation of areal production does not give more information than the P_{max} graph. It does show station 14 production in August being higher than that at stations 10 and 16. This is probably an aberration due to a deeper light penetration at station 14 on this one sampling than at the other stations.

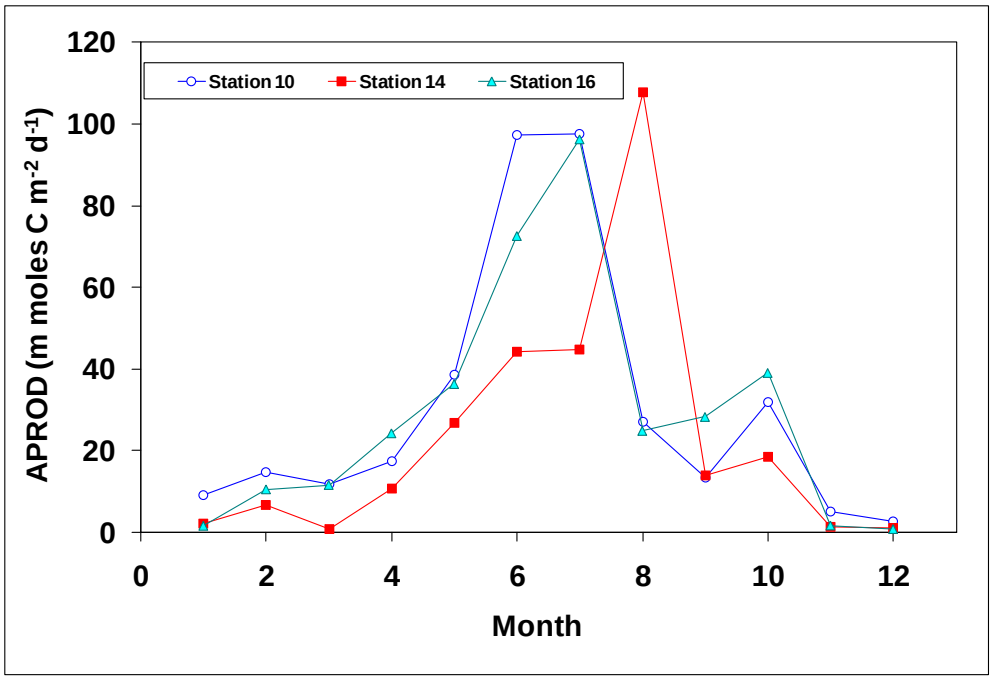

Figure 6.11. Average monthly depth-integrated areal primary production (APROD) for the most upstream station 16, wastewater treatment canal station 14, and most downstream station 10. January, February, and March values are based on single 2008 sampling; all other months are average values from 2007 and 2008 sampling.

Since a traditional concern with eutrophication is excess chlorophyll biomass, evaluation is also made of the influence of the wastewater treatment effluent on chlorophyll. The graph below shows monthly chlorophyll concentrations for the three stations. There is not as strong of a seasonal trend as is seen with primary production and there are periodic spikes at individual stations. However, there is also no indication of enhancement of chlorophyll at station 14. The average chlorophyll concentrations for all 21 samplings are 36.3 µg chlorophyll L^{-1} at station 10, 37.6 at station 16, and 21.4 at station 14. Examining all of the stations for the 21 sampling dates, chlorophyll concentrations range primarily from 5 to 100 µg L^{-1} with a few exceptional values close to 200 µ L^{-1}. The average chlorophyll concentrations for the seven stations range from only 21 to 38 µg chlorophyll L^{-1} with coefficients of variation for individual stations ranging from 60 to 100%. Overall, there is not much difference between stations.

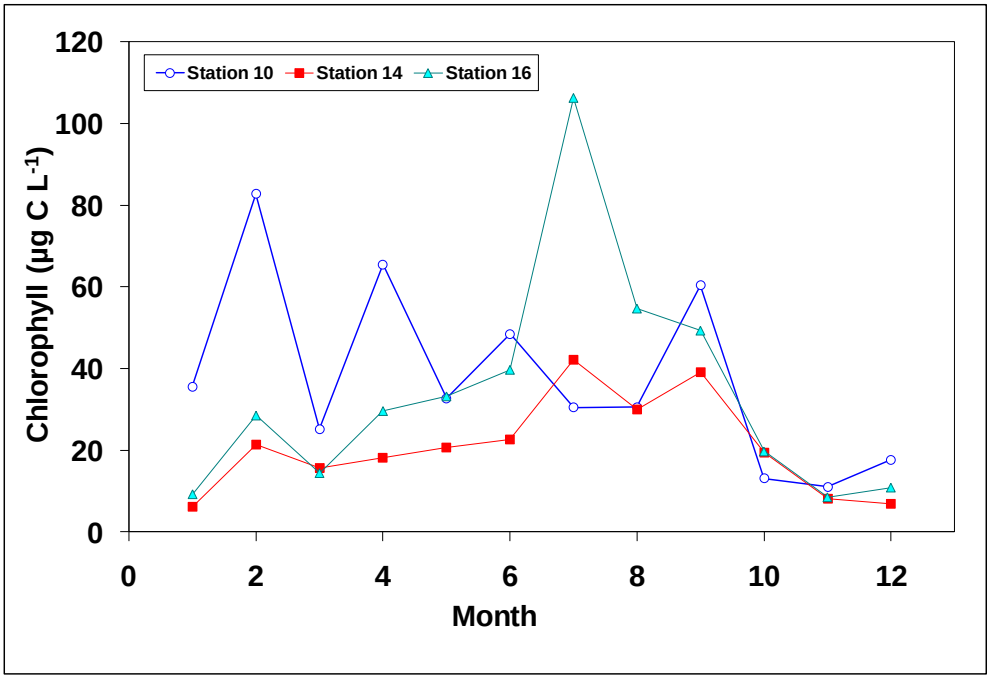

Figure 6.12. Average monthly chlorophyll concentration for the most upstream station 16, wastewater treatment canal station 14, and most downstream station 10. January, February, and March values are based on single 2008 sampling; all other months are average values from 2007 and 2008 sampling.

To analyze chlorophyll distribution more thoroughly, concentrations for each station at each of the 21 sampling times are shown in Figure 6.13. Contrasting this figure to the full distribution picture of P_{max} (Figure 6.9) even more clearly shows that chlorophyll is a poor metric for describing biological dynamics. There is a slight seasonal trend with low concentrations in October – December and higher concentrations in June-September. However, there appear to be random spikes of high chlorophyll in the period of January-May at some of the stations. High biomass can be the result of immediate high primary production, but it can also be an indicator of a slow increase in biomass due to low grazing on the primary producers. As a result, it appears that primary production is a superior indicator or the biological response to any perturbation to the system from anthropogenic inputs. From this plot of all stations and samplings, it is also emphasized that station 14 is generally lower than upstream and downstream stations. At station 14, chlorophyll rarely exceeds 30 µg L^{-1} (three values in the 50s) while at the other stations there are 38 occasions with greater than 30 µg L^{-1} chlorophyll and several near to 100 and above 100 µg L^{-1}.

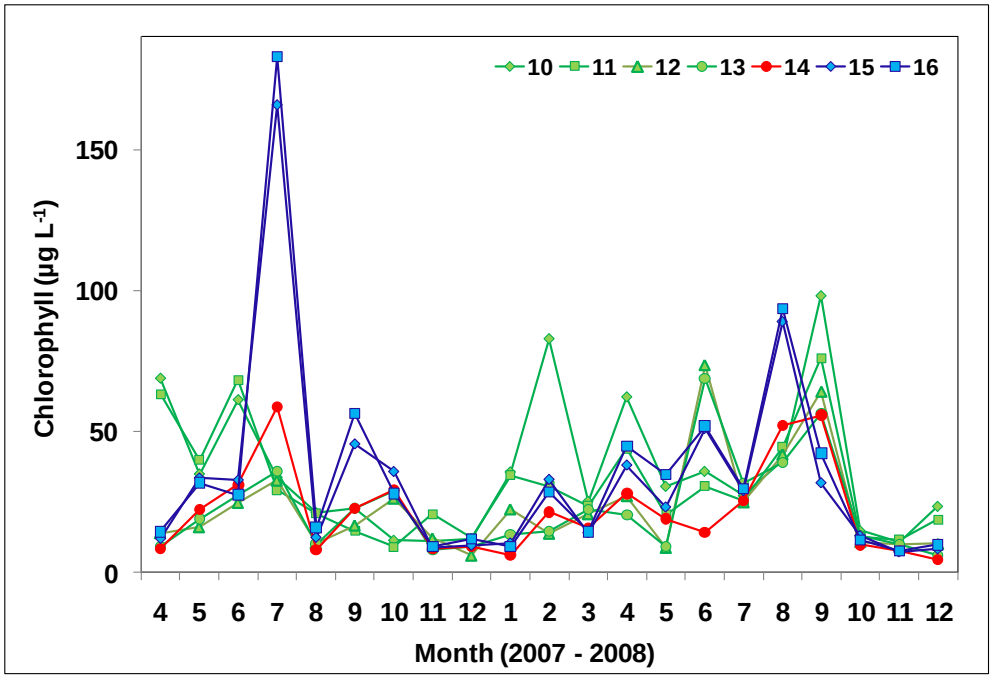

Figure 6.13. Chlorophyll concentrations for all seven stations at each sampling time from April 2007 through December 2008. Stations upstream (15 and 16) of the wastewater treatment canal have blue symbols and lines; the wastewater treatment canal (station 14) is in red; stations downstream of the canal (13, 12, 11, 10) are in green.

Normalization of production to chlorophyll biomass will give a P/B value in units of amount of carbon taken up per unit of chlorophyll. For both spatial and seasonal trends, this P/B plot can often give indication of metabolic response since variations in amount of primary producer is removed. Seasonal plots of P/B for the Delaware Estuary show large seasonal differences and indicate differing causes of limitation (Yoshiyama and Sharp, 2006). Since there appears to be a variable and non-systematic distribution of chlorophyll, as figures 6.12 and 6.13 show, P/B plots probably would not give more information than P_{max} for the Murderkill sampling. Figure 6.14 is an average monthly plot for P/B similar to those shown above for P_{max}, APROD, and chlorophyll. It does not show as clear of a seasonal cycle nor as good of a separation of stations as the P_{max} graph (Figure 6.10).

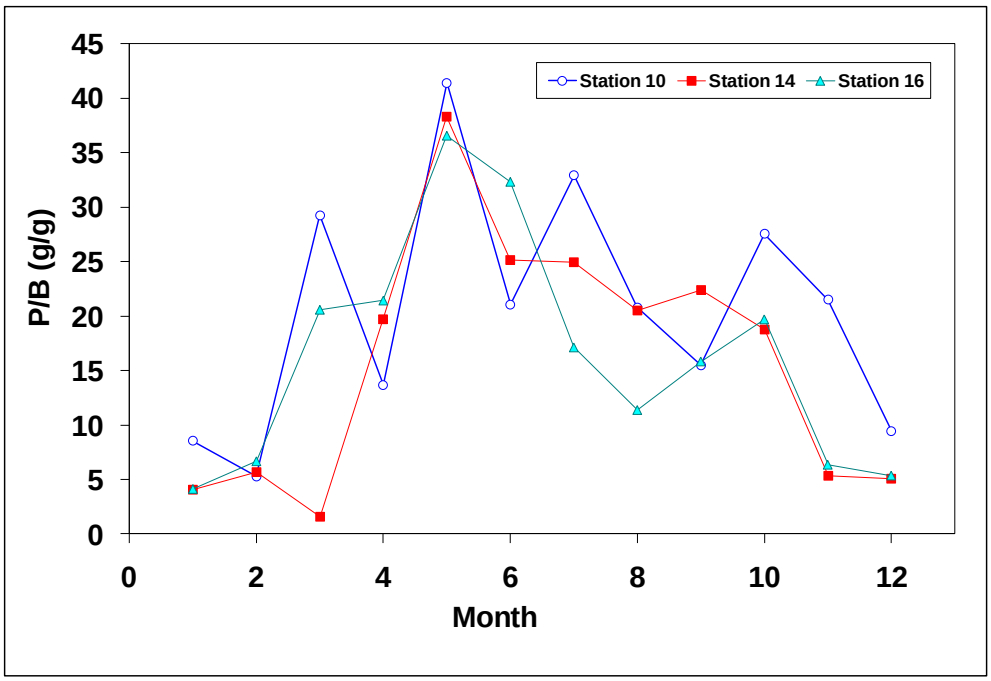

Figure 6.14. Production normalized to biomass (P/B) for the most upstream station 16, wastewater treatment canal station 14, and most downstream station 10. January, February, and March values are based on single 2008 sampling; all other months are average values from 2007 and 2008 sampling.

Further analysis of the variability of TSS and chlorophyll are shown in Table 6.1. The average TSS concentrations are very similar for all the stations and the standard deviations for each station are from 50 – 100% of the mean value. In a similar fashion, the average chlorophyll concentrations vary little from station to station and have standard deviations that range from 60 – 100%. Also, as was shown above, there is no seasonal pattern for TSS and not much of a seasonal pattern for chlorophyll.

Station	TSS		Chlorophyll	
	Mean	Std Dev	Mean	Std Dev
10	97	106	36	24
11	97	99	31	19
12	70	49	23	17
13	57	30	22	16
14	62	34	21	16
15	52	32	34	35
16	66	45	38	39

Table 6.1. Mean and standard deviation of the 21 seasonal samplings for each station for total suspended sediment concentrations (TSS, in mg L^{-1}) and for chlorophyll concentrations (µg chlorophyll L^{-1}).

There is the presumption, based on examples like Nixon and Pilson (1983), of a direct linear relationship between nutrient loading or concentration (primarily nitrogen) and algal response as biomass or primary production. This view has been contested as being too simplistic in that other primary nutrients, light, and a multitude of other factors also influence production (Cloern, 2001; Sharp, 2001; Nixon and Buckley, 2002). In turbid environments, like the Delaware Estuary, there is essentially no correlation between nitrogen concentration and primary production (Yoshiyama and Sharp, 2006; Sharp, 2010). Since the Murderkill River saline estuary is as turbid, or more turbid, than the Delaware Estuary, there is little potential for increased nutrient loading to stimulate excess primary production.

Primary production is compared to nutrient loading by plotting P_{max} against DIN (total dissolved inorganic nitrogen concentration) in Figure 6.15. As can be seen, the correlation is negative, lower production at higher nitrogen concentrations, and not strong (R^2 = 0.25). Since the highest ammonium concentrations, in saline waters, are suspect for analytical error, a graph similar to Figure 6.15 can be made using only nitrate data. That graph (not shown) had a similar slope (-0.25) and slightly lower R^2 of 0.18. While the correlation of low production at high DIN may be circumstantial (high concentrations of compounds other than DIN causing inhibition), what is clear is that there is not increased production at high nitrogen concentration; this is similar to the situation in the Delaware Estuary (Sharp, 2010).

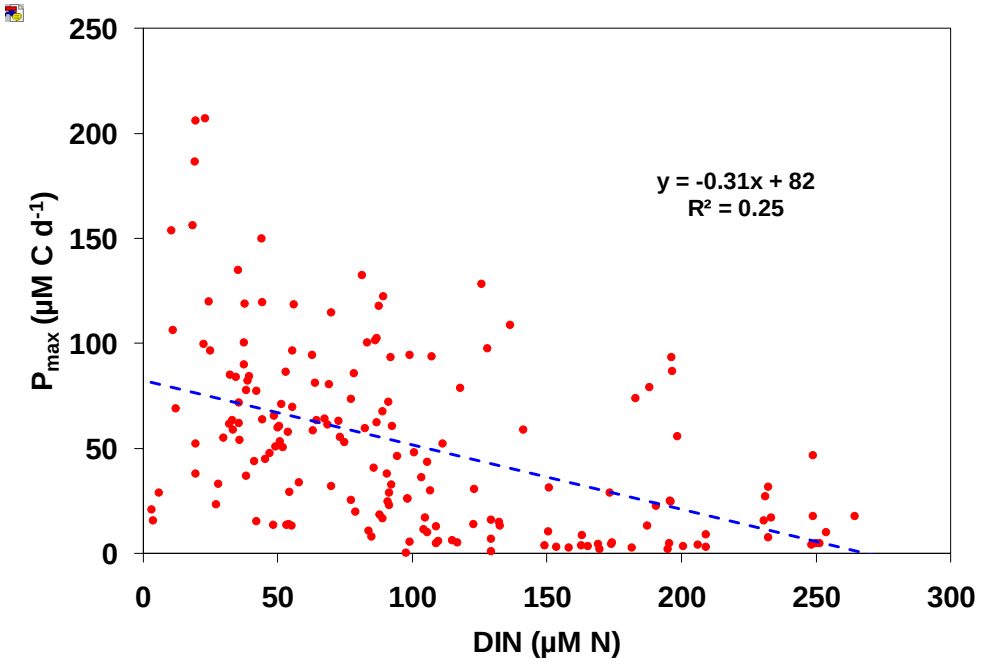

Figure 6.15. Composite plot of all P_{max} measurements against ambient total dissolved inorganic nitrogen (DIN) concentrations for the 21 samplings of the 7 stations in the Murderkill River.

At very low nitrogen concentrations, there may indeed be stimulation of primary production. Since ammonium is a preferred nitrogen source for most marine phytoplankton, P_{max} is plotted against low ammonium nitrogen concentrations in Figure 6.16. Although there are few data points in this plot (n=14), there is a positive correlation and a much better R^2 (= 0.63). Otherwise, in the vast majority of the cases (location and time), the nitrogen concentrations in the Murderkill River are too high to have a stimulatory effect on primary production.

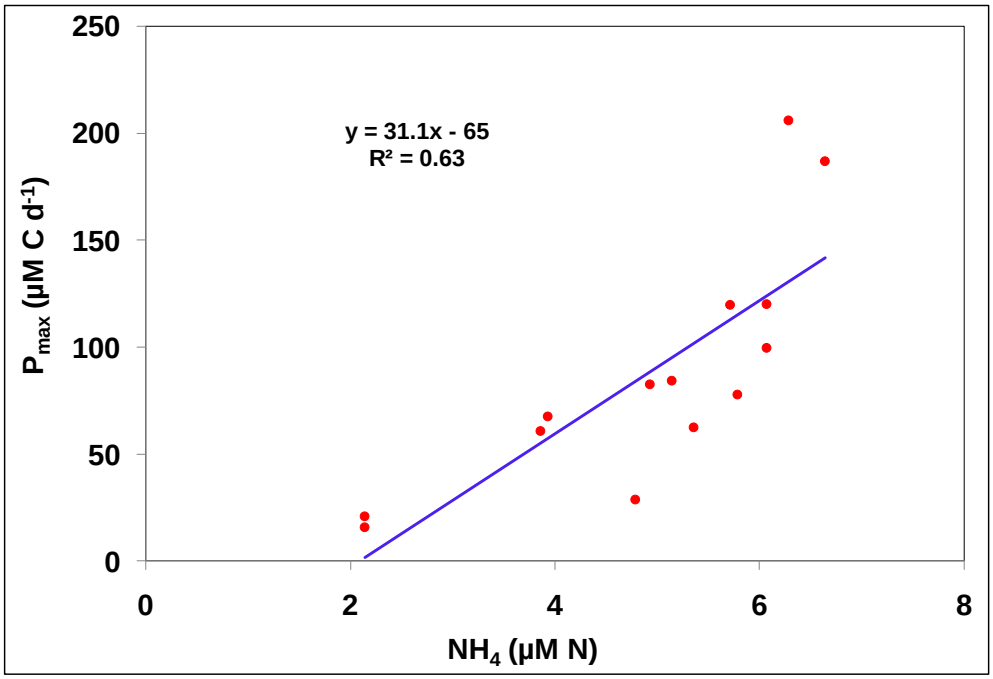

Figure 6.16. Primary production (P_{max}) versus ammonium for all stations in which the ammonium nitrogen was less than 7 µM N.

There is not a strong correlation between primary production and nitrogen concentration, so it is obvious that other factors control the rate of primary production. The plot of all primary production versus phosphate concentration (not shown) has a slightly negative slope (-0.3) but an R^2 of less than 0.01. That includes many phosphate concentrations up to 20 µM P and some up to 60 µM P. With only phosphate concentrations less than 4 µM P, there is still a negative correlation with very low R^2. Limiting the dataset to only those samples with ambient phosphate of less than 0.65 µM P, there is a positive correlation with a larger R^2 (Figure 6.17).

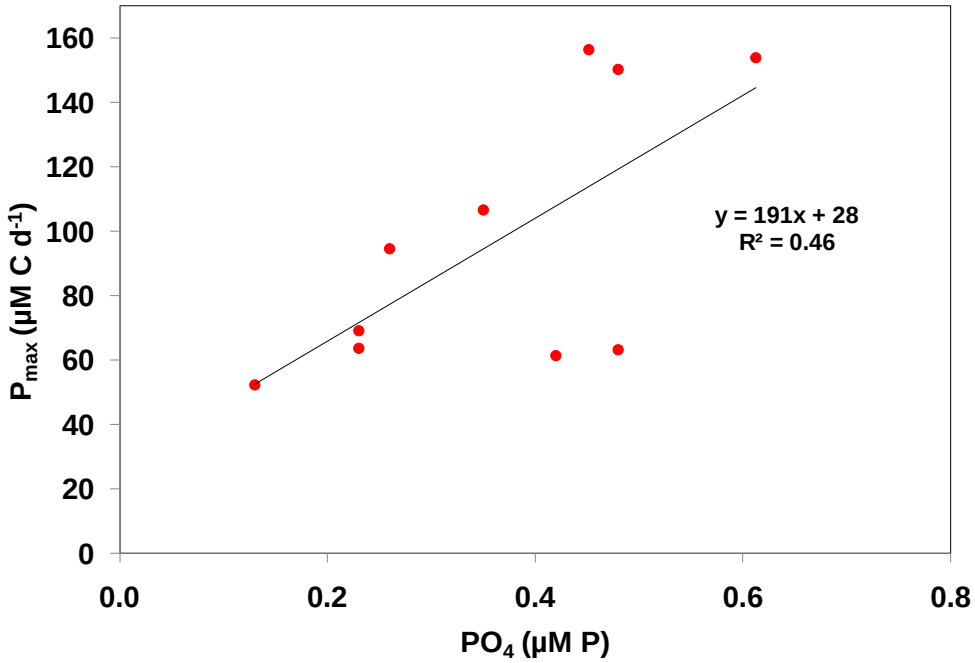

Figure 6.17. Primary production (P_{max}) versus phosphate for all stations in which the phosphate concentration was less than 0.65 µM P.

Since the Murderkill is a shallow, very turbid body of water, it is expected that light probably limits primary production. The plot of primary production (P_{max}) versus TSS (not shown) has no correlation (slope of essentially 0 and R^2<0.001). This is probably due to the fact that TSS concentrations vary rapidly with the tidal currents and hence the ambient TSS at the beginning of a 24-hr incubation should not be tightly correlated with the primary production measured over the next 24 hours. Some of the sediments settle out during the incubation and phytoplankton respond to light during the incubation period plus some acclimation to light in the period immediately prior to the incubation. Probably it is reasonable to assume that both the light "seen" by the phytoplankton for a period of 24 hours prior to the incubation plus that seen in the 24 hours of the incubation have a combined influence on the carbon assimilation. This lack of correlation of ambient TSS to P_{max} also shows why the calculation of areal production (APROD) did not add information over the measured P_{max}. While light is clearly limiting primary production, it is not easy to show the relationship in the rapidly flushing turbid Murderkill River. For all stations and sampling times measured TSS varied from about 10 to over 400 mg L^{-1}. The average TSS at each station for all 21 samplings ranged only from 52 to 97 mg L^{-1} (Table 6.1) with coefficients of variation for each station ranging from 60 – 100%. The only station trend that might be significant is that the two stations closest to the Delaware Bay (10 and 11) have higher TSS concentrations than the stations in the middle of the sampling transect (13, 14, and 15). Overall, TSS is too variable with apparently too rapid of changes to add much information about controls of the biology.

Since there is no strong correlation between nutrients and primary production, a further question might be about correlation between nutrients or primary production and dissolved oxygen concentration. A major concern in eutrophication is oxygen depletion, usually considered a result of nutrient enrichment (Nixon and Pilson, 1983; Boesch et al, 2001). The dissolved oxygen concentration is plotted against primary production for all of the summer sampling in Figure 6.18. If excess algal production were a problem, there should be a negative correlation between P_{max} and DO; instead, a slightly positive trend is seen, which is not statistically significant.

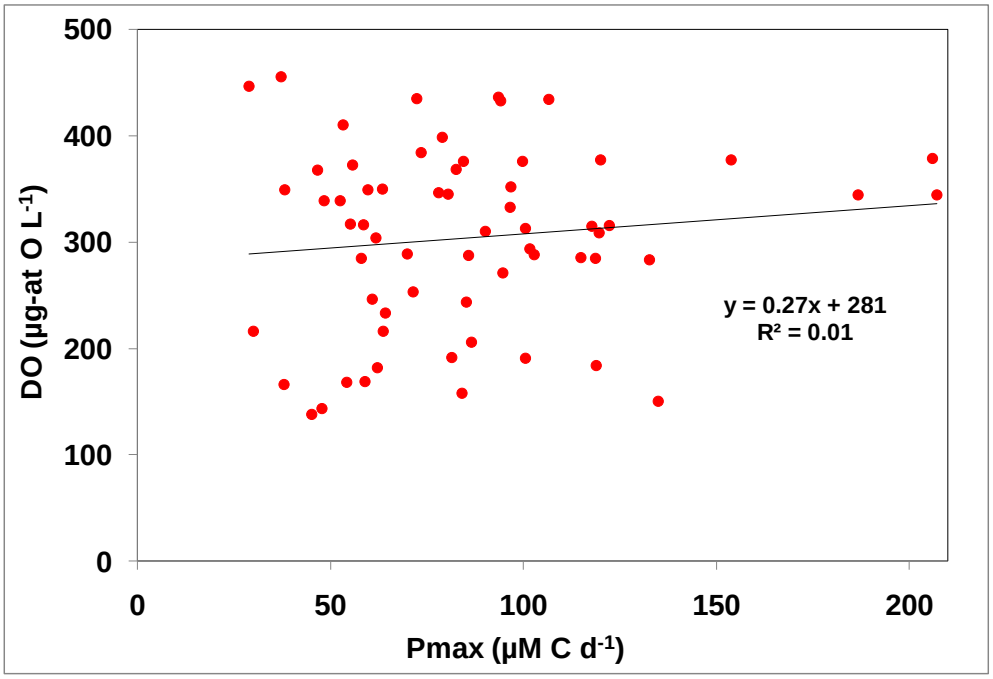

Figure 6.18. Ambient dissolved oxygen (DO) versus measured primary production (P_{max}) for all summer sampling along the Murderkill River sampling transect. DO is given in units of µg-at O L^{-1} (1 mg O_2 L^{-1} = 62.5 µg-at O L^{-1}).

A plot was also made of DO versus ammonium nitrogen. Since the high ammonium concentrations measured in salty samples were suspect, only the samples with a salinity of less than 15 ‰ were included. Also, only summer sampling is included in Figure 6.19. The plot shows a strong negative correlation between ammonium nitrogen and DO. One explanation of this correlation could be nitrification; at elevated ammonium concentration, oxidation of ammonium to nitrate in nitrification would use oxygen. The stoichiometry of nitrification gives the relationship of N:O of 1:-4 (Kaplan, 1983). The slope of the plot in Figure 6.19 is -11.2; so it is in the correct direction but is greater than what would be predicted strictly by nitrification.

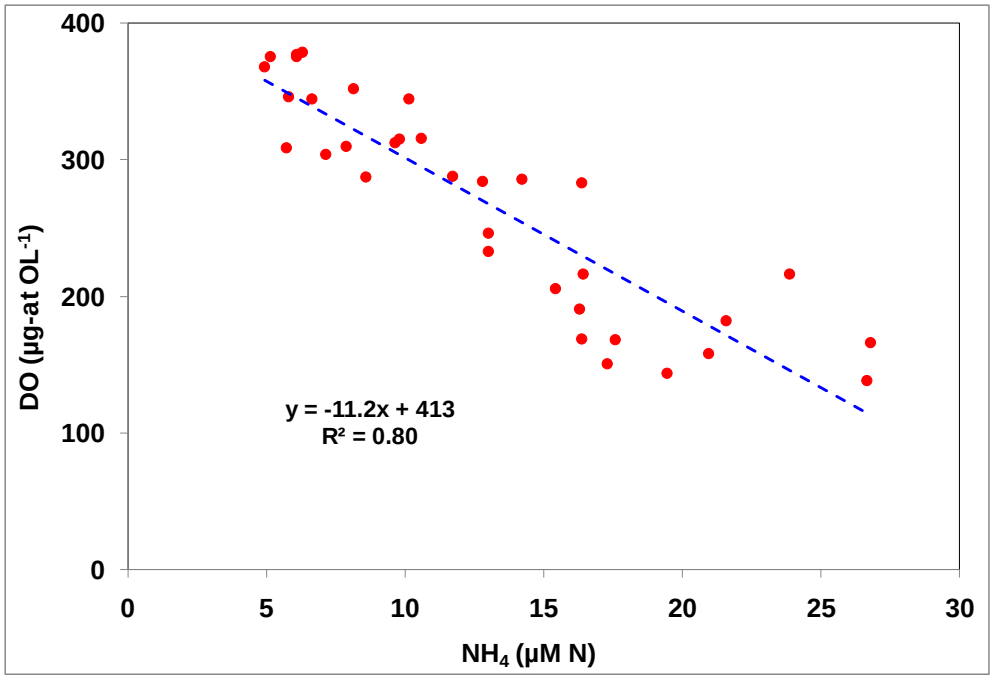

Figure 6.19. Dissolved oxygen (DO) versus ammonium nitrogen (NH_4) for summer samples along the Murderkill River sampling transect at stations where the salinity was less than 15‰.

Another reason for association of elevated ammonium and low oxygen is marsh outflow that represents a high respiration demand with elevated ammonium and decreased DO. In discussing Figure 6.8, the possibility was mentioned that excess DIC beyond what would be expected from estuarine dilution was due to respiratory input from marsh outflow. To examine this, a theoretical DIC concentration was calculated for a sample from the measured salinity using the relationship from the Delaware Bay shown in Figure 6.8; the theoretical DIC was subtracted from the measured DIC. If there is excess respiratory CO_2 in the water from respiratory demand in the marsh input, this could be represented as excess DIC. The plot of excess DIC vs DO (Figure 6.20) should show a negative correlation and a stoichiometric relationship would give a slope of -2.6 (Redfield et al, 1963). While the correlation shown in the figure is not high (R^2 = 0.22), the relationship is in the correct direction and the slope is negative. Probably the relationship of NH_4 to DO represents both input of excess NH_4 from marsh outflow and nitrification within the water of the river.

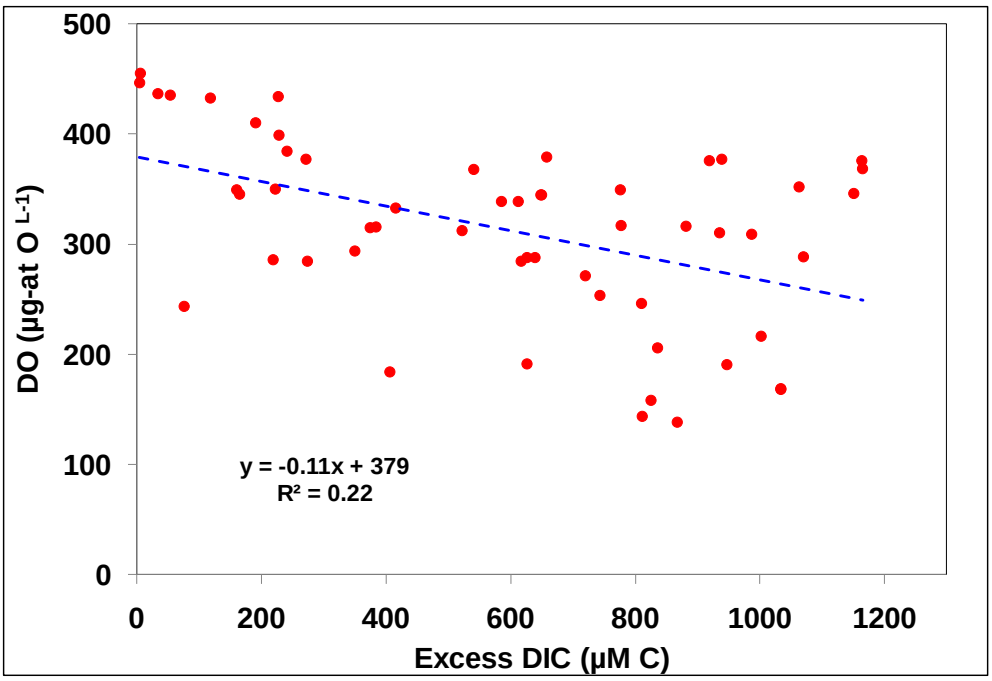

Figure 6.20. Ambient dissolved oxygen (DO) versus calculated excess dissolved inorganic carbon (DIC). The excess DIC was calculated by subtracting a theoretical DIC concentration based on salinity from the measured DIC concentration.

Conclusions

For development of TMDL criteria for the Kent County wastewater treatment plant, sampling and experiments were conducted along the Murderkill River. By evaluating conditions at station 14 (confluence of the wastewater treatment plant effluent ditch with the Murderkill River) compared to other stations, there is slight indication of nutrient enrichment. Station 14 appears to be elevated with phosphate most of the time (Figure 6.2) and proportionately less elevated with nitrate some of the time (Figure 6.3). This site is not a source of ammonium nitrogen (Figure 6.4) nor of total suspended sediment loading (Figure 6.5). While not indicative of pollution, it is somewhat surprising that station14 appears to be a source of total dissolved inorganic carbon, DIC (Figure 6.6) and of silicate (Figure 6.1). Silicate should be largely a watershed input and it shows decreasing concentration along the estuarine axis, due to dilution (Figure 6.7) as is expected. In a reverse trend, DIC, as a seawater component, shows an increase from the freshwater end of the estuary along the salinity gradient to the Delaware Bay (Figure 6.8). Both show considerable variability along the transect with diffuse input from marshes as well as input from the effluent ditch; the majority of the deviation from a linear simple dilution pattern is from the diffuse inputs along the sampling transect with a smaller portion due to the effluent ditch. Therefore, from analysis of ambient conditions along the transect from upstream to where the Murderkill River empties into the Delaware Bay, there is evidence of slight but not uniform increase of phosphate and nitrate from the wastewater treatment plant.

To test whether nutrient input from the effluent of the wastewater treatment plant had an influence on biological response in the Murderkill River, primary production was measured. The overly simplistic relationship between a single nutrient and eutrophication has been challenged with the suggestion that multiple nutrients and other factors must also be considered (Cloern, 2001; Sharp, 2001; Nixon and Buckley, 2002). Analysis of our data indicates that there is no correlation between nutrient concentration and primary production or phytoplankton biomass; this is similar to what has been found in the larger, less turbid, Delaware River and Bay Estuary (Sharp, 2010).

Recent re-assessments suggest that primary production, not chlorophyll biomass be used as a more informative indicator of eutrophication (Yoshiyama and Sharp, 2006; Smith, 2007). In our evaluation for the Murderkill River, chlorophyll, as a biomass indicator does not show elevation at Station 14. Figures 6.12 and 6.13 do not give a clear seasonal pattern anywhere along the Murderkill River nor indication of Station 14 input. Maximum primary production (P_{max}, usually at 100% light) does show a clear seasonal pattern. As with chlorophyll, there is no indication of elevation of P_{max} from the effluent ditch. In the Delaware Estuary, depth-integrated areal primary production (APROD) and production normalized to biomass (P/B) give more information about the response of the environment than does P_{max}. For the Murderkill, our study shows that APROD and P/B do not give additional information over P_{max}, but instead they blur the seasonal and station trends. The reason that APROD does not add information Figure 6.11) is undoubtedly due to the fact that the light attenuation from TSS is highly

variable, probably at a subtidal frequency and hence there is no station nor seasonal trend (Table 6.1). The failure of information from P/B (Figure 6.14) is probably due to the fact that the chlorophyll is quite variable with minimal seasonal and essentially no station trend (Figure 6.13, Table 6.1).

There appears to be no correlation between nutrient concentration and primary production (Figure 6.15). At the lowest measured nutrient concentrations, a stimulation of primary production from ammonium nitrogen (Figure 6.16) and phosphate (Figure 6.17) does appear; usually at the highest salinity station nearest the Delaware Bay.

Since a concern in eutrophication is depletion of dissolved oxygen, this has also been evaluated. A typical paradigm is increased algal production from elevated nutrients provides excess organic matter that is respired decreasing dissolved oxygen. Since the Murderkill River system flushes rapidly and is well mixed from top to bottom, the potential for oxygen depletion from excess algal production is not as great as that in an aquatic system that has more isolated waters. A plot of primary production versus ambient dissolved oxygen does not show the expected negative correlation of this paradigm (Figure 6.18). A plot of dissolved oxygen versus low ammonium concentration (at low salinity) shows the expected negative correlation that could indicate oxygen demand from nitrification (Figure 6.19). It is also possible, that this correlation indicates both oxygen depletion and ammonium elevation from high respiratory activity in marsh outflow waters. A plot of excess DIC versus DO confirms this possibility (Figure 6.20).

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